Chapter IV

SYNTHESES AND CHARACTERIZATION OF PANI- \( \text{RuO}_2 \) COMPOSITE THIN FILMS BY SILAR METHOD AND THEIR SUPERCAPACITOR AND GAS SENSOR PERFORMANCE
## Chapter IV

**SYNTHESIS AND CHARACTERIZATION OF PANI- RuO$_2$ COMPOSITE THIN FILMS BY SILAR METHOD AND THEIR SUPERCAPACITOR AND GAS SENSOR PERFORMANCE**

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Section A

Synthesis and Characterization of PANI-RuO$_2$ Composite Thin Films by SILAR Method

4.A.1 Introduction

The successive ionic layer adsorption reaction (SILAR) method has become the prime choice for fabrication of nanostructured films in which synergy between distinct materials may be achieved in a straightforward, low-cost manner. A wide diversity of materials like chalcogenides, mixed metal chalcogenide and oxides may be employed and film fabrication is performed under mild conditions [1-6]. Among such materials the deposited films have the various applications, including in photoelectrochemical cell [7, 8], dye sensitized solar cell [9], gas sensor, and supercapacitor [10, 11], etc.

The present section deals with the synthesis of PANI-RuO$_2$ composite film on conducting and nonconducting substrates by means of SILAR method. The prepared PANI-RuO$_2$ composite thin films are further characterized and studied for crystal structure, morphology, FT-IR, FT-Raman, Optical and wettability study.

4.A.2 Experimental Details

4.A.2.1 Experimental Setup for Deposition of PANI-RuO$_2$ Composite Thin Films

In the present work, the synthesis process of PANI-RuO$_2$ composite thin films by SILAR method is based on the immersion of substrates into the cationic and anionic precursors. Fig. 4.1 (a) shows the schematic presentation of SILAR method for deposition of PANI-RuO$_2$ composite thin film. Fig. 4.1 (b) shows the computer interfaced SILAR unit for the deposition of the PANI-RuO$_2$ composite thin films. Four beakers system is used for the deposition of PANI-RuO$_2$ composite thin films. The first beaker contains 0.1 M aniline monomer dissolved in 1 M sulfuric acid which serves as the anilinium cations (anilinium salts) source and the second beaker contains 0.1 M ammonium per sulphate (APS) dissolved in the 1 M sulfuric acid serves as the oxidizing agent and hydrogen sulfate anions as an anionic precursor source. The third beaker contains aqueous RuCl$_3$·xH$_2$O (0.01M) kept at room temperature (300 K) and used as cationic precursor. The anionic
precursor was double distilled water at 333 K temperature placed in fourth beaker. In this method, substrates were immersed alternatively in the separately ion carrying precursor solutions with regular interval. Initially, the substrate was immersed in the cationic precursor solution for 10s to adsorb aniline ion on the substrate. After that, the substrate was immersed in the second ammonium persulphate anionic precursor solution for 10s to react with aniline cation to form a layer of PANI on the substrate. Then the PANI coated substrate was immersed in the third beaker containing cationic precursor solution 20s to adsorb the ruthenium ions. After that substrate was immersed in the anionic precursor solution i.e. double distilled water placed at 333 K for 40s. The reaction occurs with OH\(^-\) ions from anionic precursor to form \(\text{RuO}_2\) on the PANI coated substrate. Thus, it completes the one SILAR cycle for the deposition of PANI-RuO\(_2\) composite thin film. This cycle was repeated for several times in order to increase the overall film thickness of PANI-RuO\(_2\) composite thin film. The period for which the substrate was kept in cationic bath is referred as adsorption period and that for which kept in anionic bath was referred reaction period. The preparative parameters for the PANI-RuO\(_2\) composite thin films are given in Table 4.1

<table>
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<th>Table 4.1: Optimized preparative parameters for the deposition of PANI-RuO(_2) composite.</th>
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<tr>
<td><strong>Cationic precursor</strong></td>
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<td><strong>Anionic precursor</strong></td>
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<tr>
<td><strong>Adsorption time</strong></td>
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<tr>
<td><strong>Reaction time</strong></td>
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<tr>
<td><strong>No. of immersion cycles</strong></td>
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<td><strong>Substrates</strong></td>
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Fig. 4.1 (a): Schematic representation of the SILAR method for the PANI-RuO₂ composite thin films.

Fig. 4.1 (b): Photograph of computer interfaced SILAR unit for the deposition of PANI-RuO₂ composite thin films [1st and 3rd beakers contain cationic and 2nd and 4th beakers contain anionic solutions].

4.A.2.2 Characterization Techniques

The PANI-RuO₂ composite films were characterized for structural, surface morphological, wettability and optical properties using the techniques described in section 3.A.2.3.
4.3 Results and Discussion

4.3.1 PANI-RuO$_2$ Composite Thin Film Formation and Reaction Mechanism

The PANI-RuO$_2$ composite thin film formation mechanism by SILAR method is explained in the two steps. The first step gives the formation of PANI thin film on the substrate. The formation of RuO$_2$ on the precoated PANI thin film is given in the second step.

**Step I:** The aniline monomer cations present in the acidic bath of first beaker, adsorbed on the substrate surface and further these anilinium cations reacts with oxidizing ammonium persulphate in the second beaker resulting into formation of emeraldine form of PANI. In this case, hydrogen atoms preoccupied from aniline molecules during their blending to oligomeric and polymeric structures are released as protons, i.e. sulfuric acid as a by-product. The reaction mechanism for the PANI thin film formation is explained by equation 3.3 in the chapter III.

**Step II:** The general reaction mechanism for RuO$_2$ film formation on PANI coated substrates by SILAR can be described as follows. The ruthenium (III) chloride precursor solution provides the Ru$^{3+}$ cations for the reaction. These cations get adsorbed on the immersed substrate due to some attractive forces between ions in the solution. The forces of attraction which are responsible for adsorption of ions on substrate may be cohesive forces or Van-der-Walls forces or chemically attractive forces [12].

The substrate is then immersed in double distilled water (333 K), where the OH- anions combine to form ruthenium hydroxide (Ru(OH)$_3$). In next step the excess anions reacting with ruthenium hydroxide to convert it into ruthenium oxide. The reaction for RuO$_2$ film formation can be represented as,

\[
\begin{align*}
2 \text{Ru(III)}\text{Cl}_3 &\rightarrow 2 \text{Ru}^{3+} + 3 \text{Cl}_2 \uparrow \\
\text{Ru}^{3+} + 3 \text{OH}^- &\rightarrow \text{Ru(OH)₃} \\
\text{Ru(OH)₃} + \text{OH}^- &\xrightarrow{Δ} \text{RuO₂} + 2\text{H₂O}
\end{align*}
\]

The well adherent and greenish black films of PANI-RuO$_2$ composite were formed on the glass and stainless steel substrates. The thickness of these films was increased by increasing deposition cycles.
4.A.3.2 Thickness Measurement

The thickness of deposited PANI-RuO$_2$ composite thin film on stainless steel and glass substrate was measured using traditional weight difference method described in section 3.A.3.2. The variation of the weight of PANI-RuO$_2$ composite thin film deposited on the substrate with the number of immersion cycles is shown in Fig 4.2. It was observed that the PANI-RuO$_2$ composite film thickness increased with an increase in the number of immersion cycles. The terminated thickness, at which the highest amount of PANI-RuO$_2$ composite is deposited on the stainless steel substrate, is 0.14 mg.cm$^{-2}$ at 50 cycles and that of glass substrate is 0.11 mg.cm$^{-2}$. The slight decrease in film thickness observed after 50 cycles is attributed to the formation of outer porous layer and/or the film which may develop stress to cause delimitation resulting in peeling off the film after the film reaches at maximum thickness [13]. The initial nucleation growth rate on the crystalline substrates is higher than the amorphous substrates, and therefore the PANI-RuO$_2$ composite thin film has the more thickness on the stainless steel substrate than the amorphous glass substrate [14].

Fig. 4.3 shows the photographs of (a) RuO$_2$, (b) PANI-RuO$_2$ composite and (c) PANI thin films on the stainless steel substrates having the area > 10 cm$^2$. It is observed from the photographs that the RuO$_2$ thin film is slightly blackish in color, PANI-RuO$_2$ composite thin film color is greenish black that of different from green PANI color. Also greater deposited area shows that the SILAR method can be applied for large area deposition of thin films.
**Fig. 4.2:** Variation of PANI-RuO$_2$ composite film thickness with no. of immersion cycles on the (a) stainless steel and (b) glass substrates.

**Fig. 4.3:** Photographs of the (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin films on the stainless steel substrate.

**4.A.3.3 X-ray Diffraction Study**

The XRD patterns were recorded in the 2$\theta$ range of 10 to 100$^0$ to study the structural analysis of the RuO$_2$, PANI-RuO$_2$ composite and PANI thin films. Fig. 4.4 shows the X-ray diffraction patterns of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin films on stainless steel substrate. The peaks observed in the XRD
patterns are due to stainless steel substrate [15] and there is no diffraction peak corresponding to PANI-RuO$_2$ composite indicating that the PANI-RuO$_2$ composite has an amorphous characteristic (Fig. 4.4 (b)). The amorphous thin film structure is more desirable due to the relatively flexible intercalation-deintercalation of H$^+$ and OH$^-$ ions than in the crystalline phase [16]. Also the Fig. 4.4 (a and c) shows the amorphous nature of the RuO$_2$ and PANI thin films on the stainless steel substrate, respectively.

**Fig. 4.4**: X-ray diffractograms of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin films on stainless steel substrate.

**4.A.3.4 Surface Morphological Study**

Fig. 4.5 (a) shows the scanning electron micrographs of the RuO$_2$ thin film on the stainless steel substrate at 10,000 X, magnification. The SEM analysis showed that RuO$_2$ was deposited in the form of nanoparticles forming undernourished structure and relatively featureless surface with no observable homogeneity. It is observed that nanoparticles grouped together to form highly porous network agglomerates. Further, these agglomerates consist of smaller irregularly shaped nano particles [17].
Fig. 4.5 (b) shows the scanning electron micrograph of the PANI-RuO$_2$ composite thin film at 10,000 x magnification. It shows that PANI-RuO$_2$ composite was deposited in the form of nanofibrils with relatively porous structure on the stainless steel substrate having the diameter in the range of 200 to 300 nm.

Fig. 4.5 (c) shows the scanning electron micrograph of the PANI thin film at 10,000 x magnification. It is observed that the PANI nanofibers appear to laid down on the substrate as a kind of hierarchically interrelated structure. Furthermore, image of the PANI film shows the highly porous network of nanofibres with the diameter of the ~ 200 nm.

Fig. 4.5 (d, e, and f) shows the SEM images of RuO$_2$, PANI-RuO$_2$ composite and PANI thin films at 10,000 x magnification on the glass substrate, respectively. The SEM image of RuO$_2$ shows the total coverage of the substrate and seems to be peeled off from substrate surface. PANI-RuO$_2$ composite SEM (Fig. 4.5 e) shows the bunch of agglomerated dwarf nanorods with porous structure. It is clear that the nanofibres have the diameter ranging from 100 to 200 nm. From the Fig. 4.5 (f), one can clearly observe the smooth surface of PANI thin film with some overgrowth bunch of agglomerated irregularly shaped particles.
Fig. 4.5: SEM micrographs of (a) RuO₂, (b) PANI-RuO₂ composite, and (c) PANI thin films on stainless steel and (d) RuO₂, (e) PANI-RuO₂ composite, and (f) PANI thin films on glass substrates, at 10,000 x magnification.

4.4.3.5 Wettability Study

The phenomena of wetting or non-wetting of a solid by liquid is better understood by studying the contact angle measurement. Fig. 4.6 shows the surface wettability of the (a) RuO₂, (b) PANI-RuO₂ composite, and (c) PANI thin films evaluated by means of water contact angle measurement. The water contact angle measurement showed hydrophilic nature of (a) RuO₂, (b) PANI-RuO₂ composite,
and (c) PANI thin films with water contact angle $70^0$, $25^0$, and $12^0$ on stainless steel substrate, respectively. The films are hydrophilic due to the porous structure of the material deposited on the substrate which is revealed from the surface morphology [18]. Hydrophilic nature is useful for making close contact of aqueous electrolyte with film surface in supercapacitor application. It is well known that in electrochemical supercapacitor, hydrophilic surface of the electrode is an essential factor for better performance [16]. The surface energies of thin films were calculated using the Neumann's equation of state [19]. The surface energies of (a) RuO$_2$ (b) PANI-RuO$_2$ composite and (c) PANI thin films are found to be 40.76, 65.97 and 70.47 mJ/m$^2$, respectively.

**Fig. 4.6:** Measurement of water contact angles of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin films on stainless steel substrate.

4.A.3.6 Fourier Transform Infrared (FT-IR) Spectroscopy Study

The FT-IR study was performed in order to identify the presence of bending or stretching vibrations in the synthesized thin films. The FT-IR absorption spectra of (a) RuO$_2$, (b) PANI-RuO$_2$ composite and (c) PANI thin films
synthesized using SILAR method are shown in Fig. 4.7. Fig. 4.7 (a) shows the FT-IR spectrum of RuO₂. The small peak observed at 616 cm⁻¹ is a characteristic vibrational mode of rutile RuO₂ [20]. The small absorption band around at 1109 cm⁻¹ is assigned to characteristic stretching vibration of peroxo groups [21]. The absorption band around at 1634 cm⁻¹ is due to the bending vibration of hydroxyl groups of molecular water [22]. The broad absorption band around at 3425 cm⁻¹ is attributed to the stretching vibrations of OH [23].

Fig. 4.7 (b) shows the spectrum of PANI-RuO₂ composite thin film. The characteristic vibrational mode of rutile RuO₂ band is shifted from 616 cm⁻¹ for pure RuO₂ to the 630 cm⁻¹ in PANI-RuO₂ composite thin film [24, 25]. The band at 811 cm⁻¹ is attributed to the out-of-plane C-H bending modes. The strong band at 1117 cm⁻¹ in pure PANI is shifted to the 1152 cm⁻¹ for PANI-RuO₂ composite thin film which is the stretching mode of N=Q=N, and is considered to be a measure of the degree of electron delocalization [26]. Both the spectrum (b) PANI-RuO₂ and (c) PANI shows the C-N stretching peak of the secondary aromatic amine around 1301 cm⁻¹, however the less intensity is observed in case of PANI-RuO₂ composite thin film [25, 27]. The characteristic band of benzene ring (B) structure at 1498 cm⁻¹ of PANI is shifted to the 1477 cm⁻¹ for PANI-RuO₂ composite thin film as well as the band of nitrogen quinine (Q) structure at 1591 cm⁻¹ of PANI is shifted to 1580 cm⁻¹ in PANI-RuO₂ composite thin films [28]. The less intense peak at 2931 cm⁻¹ is assigned to the free N-H stretching vibrations of secondary amines and vibration associated with the NH²⁺ part in the −C₆H₄NH²⁺C₆H₄− group in PANI-RuO₂ spectrum [29]. The weak and broad band at 3427 cm⁻¹ is assigned to N-H stretching mode in PANI spectrum [30].

Thus the FT-IR study confirms the formation of PANI-RuO₂ composite thin films. The shift in characteristic band positions of the PANI in the PANI-RuO₂ composite shows that there is strong interaction of RuO₂ particles with PANI chain.
4.4.3.7 FT-Raman Study

Raman spectrum is a powerful means of researching the interaction between substrate surface and the absorbed materials. FT-Raman spectra of RuO$_2$, PANI-RuO$_2$ composite and PANI thin films are showed in Fig. 4.8 (a), (b) and (c), respectively. The Raman spectrum of RuO$_2$ (Fig. 4.8 (a)) showed three Raman peaks at 520, 630 and 703 cm$^{-1}$ corresponding to the $B_{1g}$, $A_{1g}$ and $B_{2g}$ vibration modes of RuO$_2$ [31].

Fig. 4.8 (c) shows the Raman spectrum of PANI thin film. The characteristic five Raman peaks are observed at 1165, 1265, 1328, 1510 and 1585 cm$^{-1}$ [32]. The PANI-RuO$_2$ composite Raman spectrum (Fig. 4.8 (b)) shows the less intense characteristic Raman peaks of RuO$_2$ and characteristic Raman peaks of PANI with some shift in wavenumber. This may be due the interaction of PANI and RuO$_2$ material. Thus the FT-Raman study supports to the FT-IR study for the composite confirmation of PANI-RuO$_2$ composite thin film [33, 34].
**Fig. 4.8:** FT-Raman spectra of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin films.

**4.A.3.8 Optical Study**

Fig. 4.9 shows the variation of optical absorbance ($\alpha t$) of (a) RuO$_2$ (b) PANI-RuO$_2$ composite and (c) PANI thin films studied in 350–750 nm wavelength range.

The optical absorption spectrum of PANI-RuO$_2$ composite thin film is shown in Fig. 4.9 (b). The spectrum shows the optical edge at 480 nm. This edge is higher than the optical edge 460 nm of PANI (Fig. 4.9 c). The small absorption peak at 440 nm for PANI thin film disappers in the PANI-RuO$_2$ composite thin film indicating that the interaction of RuO$_2$ and PANI chain [35]. Also at higher wavelength, absorption of PANI-RuO$_2$ thin composite decreases like the absorption of RuO$_2$ thin film.
**Fig. 4.9:** Absorption spectra of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin films.

**4.A.3.9 Conclusions**

The amorphous PANI-RuO$_2$ composite thin films have been synthesized by simple and inexpensive SILAR (successive ionic layer adsorption and reaction) method. The surface morphology reveals the porous nature of the PANI-RuO$_2$ composite thin film with nanofibrils with the diameter in the range of 250-500 nm. The formation of PANI-RuO$_2$ was confirmed from the FT-IR and FT-Raman studies. Also the optical study supports the composite formation of PANI-RuO$_2$ thin film. The PANI-RuO$_2$ composite films showed hydrophilic nature.
Section B

Supercapacitive Performance of PANI–RuO₂ Composite Thin Films

4.B.1 Introduction

Supercapacitors have attracted great interest as promising energy storage devices due to their higher power energy density and longer cycle performance than conventional dielectric capacitors. Supercapacitors are now widely used in hybrid electric vehicle along with the improvement in transportation field [36, 37]. It is clear that the performances of capacitors mainly depend on the properties of the electrode materials. Current research has been centered mainly on conducting polymers such as polyaniline, polypyrrole, polythiophene with metal oxides [38, 39]. Amongst conducting polymers, polyaniline has received a significant amount of attention due to its simple doping/dedoping chemistry and promising electrical, electrochemical, optical properties [40].

In this section, PANI-RuO₂ composite thin films have been studied for the supercapacitor application with cyclic voltammetry, charge-discharge, and electrochemical impedance techniques. Further, the stability of the PANI-RuO₂ composite was studied and the comparison of supercapacitive properties between RuO₂, PANI-RuO₂ composite, and PANI thin films has been made.

4.B.2 Results and Discussion

4.B.2.1 Cyclic Voltammetry Study

Cyclic voltammetry (CV) technique was used to investigate the supercapacitive properties of the RuO₂, PANI-RuO₂ composite and PANI thin film electrodes. The CV curves of the RuO₂, PANI-RuO₂ composite and PANI thin films are shown in the Fig. 4.10 (a), (b) and (c), respectively. The CV curves of RuO₂ were obtained in the potential window of 0 to +1 V vs SCE whereas positive CV curves of PANI-RuO₂ and PANI thin film were studied in the potential window of -0.2 to +0.8 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 5 mV.s⁻¹ scan rate. The CV curve of RuO₂ shows pseudocapacitive behavior in the potential window 0 to +1 V vs SCE. The CV curves of PANI and PANI-RuO₂ thin films show the pseudocapacitive behavior of the PANI and PANI-
RuO₂ composite electrode which is a distinct from that of the electric double-layer capacitance [41]. The appearance of single pair of redox peaks indicates that the PANI-RuO₂ composite gives rise to pseudocapacitance of the electrode [42, 43].

The CV curve of PANI shows the two pairs of redox peaks (A₁/A₂) and (B₁/B₂) which are indicative of typical pseudocapacitive characteristic of PANI. Peaks (A₁/A₂) are ascribed to the redox transition of PANI from leucoemeraldine to emeraldine form [44]. Faradic transformation from emeraldine pernigraniline is responsible for peaks (B₁/B₂) [44]. The CV curve of PANI-RuO₂ composite shows the disappearance of second pair redox peaks (B₁/B₂), which may be due to the RuO₂ particle interaction. The higher CV current of PANI thin film electrode is due to the porous network of nanofibres and more hydrophilic nature.

![Graph showing CV curves of different electrodes](image)

**Fig.4.10:** The CV curves of (a) RuO₂, (b) PANI-RuO₂ composite, and (c) PANI electrodes.

4.B.2.2 Effect of Film Thickness

The thickness effect of the PANI-RuO₂ composite electrode on the supercapacitive behavior was studied in 1 M H₂SO₄ electrolyte at the scan rate of 5 mV.s⁻¹. Fig. 4.11 shows the cyclic voltammetric curves of PANI-RuO₂ composite electrode with different thicknesses. It is observed that area under curve increases as the thickness increases up to thickness 0.14 mg.cm⁻². Therefore, the PANI-RuO₂
composite electrode showed maximum capacitance of 664 F.g\(^{-1}\) at 0.14 mg.cm\(^{-2}\) thickness.

![Graph showing CV curves for different thicknesses](image)

**Fig. 4.11:** The thickness dependent CV curves of PANI-RuO\(_2\) composite electrode at the scan rate of 5 mV.s\(^{-1}\).

The variations of interfacial and specific capacitances with thickness are given in Table 4.2. It is seen that as the thickness increased from 0.05 to 0.14 mg.cm\(^{-2}\), the interfacial capacitance increased from 0.009 to 0.09 F.cm\(^{-2}\) and specific capacitance increased from 185 to 664 F.g\(^{-1}\).

<table>
<thead>
<tr>
<th>Thickness (mg.cm(^{-2}))</th>
<th>Specific Capacitance (F.g(^{-1}))</th>
<th>Interfacial Capacitance (F.cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>185</td>
<td>0.009</td>
</tr>
<tr>
<td>0.11</td>
<td>498</td>
<td>0.054</td>
</tr>
<tr>
<td>0.14</td>
<td>664</td>
<td>0.093</td>
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**Table 4.2:** The effect of film thickness on the specific and interfacial capacitances of PANI-RuO\(_2\) composite electrode.

**4.B.2.3 Effect of Scan Rate Variation**

The cyclic voltammetric (CV) curves of PANI-RuO\(_2\) composite electrode at different scan rates are shown in Fig. 4.12. The area under curves was slowly increased with the scan rate. The cyclic voltammograms at high scan rates do not
show redox peaks over the potential range because the proton transfer process is slow at higher scan rate and it leads to either depletion or saturation of the protons in the electrolyte inside the electrode during the redox process. This mainly results in the increase of ionic resistivity leading to drop in the capacitance of the electrode [40].

Fig. 4.12: The CV curves of PANI-RuO₂ composite thin film at various scan rates.

Fig. 4.13 shows the variation of specific capacitance of (a) RuO₂, (b) PANI-RuO₂ composite and (c) PANI thin films with scan rates. 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 5 mV.s⁻¹, maximum specific capacitance is found to be 664 F.g⁻¹. Fig. 4.14 shows the variation of interfacial capacitance with scan rate of the (a) RuO₂, (b) PANI-RuO₂ composite, and (c) PANI thin films. It is observed that the as scan rate increases the interfacial capacitance decreases.
**Fig. 4.13:** The effect of scan rate on specific capacitance of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin film electrodes.

**Fig. 4.14:** The effect of scan rate on interfacial capacitance of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin film electrodes.

### 4.B.2.4 Stability Study

The stability and reversibility of an electrode material are important for its use in an electrochemical supercapacitor. Stability of PANI-RuO$_2$ composite electrode was tested by cyclic voltammetry. Fig. 4.15 shows the CV curves of PANI-
RuO₂ composite electrode at the scan rate of 100 mV.s⁻¹ within the voltage range -0.2 to +0.8 V vs. SCE for 1st and 5000th number of cycle. The current under curve is decreased by 11% up to 5000 cycles. We found that our system can withstand about 5000th cycles without a significant decrease in the supercapacity, illustrating the fairly stable (89%) nature of PANI-RuO₂ composite 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 [45].

![Graph showing CV curves of PANI-RuO₂ composite thin film electrode at 1st and 5000th cycles.](image)

**Fig. 4.15:** The CV curves of PANI-RuO₂ composite thin film electrode at 1st and 5000th cycles.

Fig. 4.16 shows the comparative stability study of (a) RuO₂ (b) PANI-RuO₂ composite and (c) PANI thin films. Fig. 4.16 (a) shows the 79% stability of RuO₂ over the 5000th cycles. The PANI thin film showed 70% stability (Fig. 4.16 (c)). The PANI-RuO₂ composite thin film showed the 89% stability over the 5000th cycles (Fig. 4.16 (c)). It is observed that the composite material showed the excellent stability over the 5000th cycles as compared to pure materials. These results reveal that the introduction of RuO₂ prevents the PANI from mechanical changes (shrinkage and breaking) during long cycling, and enjoys high stability of the composite electrode for long cycle life.
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Fig. 4.16: The variation of specific capacitance as a function cycle number for (a) RuO\(_2\), (b) PANI-RuO\(_2\) composite, and (c) PANI thin film electrodes.

4.B.2.5 Charge-Discharge Study

The charge–discharge behavior of the RuO\(_2\), PANI-RuO\(_2\) composite and PANI thin films was examined by chronopotentiometry in the potential range of -0.2 to +0.8 V vs. SCE at 0.5 mA.cm\(^{-2}\) current density. The charge-discharge curves of RuO\(_2\), PANI-RuO\(_2\) and PANI thin films are shown in Fig. 4.17 (a), (b) and (c), respectively. The charge-discharge curve of (a) RuO\(_2\) shows the approximately linear charge and discharge time, while there is a potential drop observed in case of (b) PANI-RuO\(_2\) and (c) PANI during discharging time when the potential is reversed. The PANI-RuO\(_2\) composite electrode shows a higher potential drop than the PANI electrode. The supercapacitor parameters such as specific power (SP), specific energy (SE) and coulombic efficiency (\(\eta\)) are calculated using the relationships described in section 3.B.2.3 and are shown in Table 4.3,

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Materials</th>
<th>RuO(_2)</th>
<th>PANI-RuO(_2)</th>
<th>PANI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Power (S.P.) in KW.kg(^{-1})</td>
<td></td>
<td>1.70</td>
<td>3.57</td>
<td>0.78</td>
</tr>
<tr>
<td>Specific Energy (S.E.) in Wh.kg(^{-1})</td>
<td></td>
<td>12.89</td>
<td>432</td>
<td>143</td>
</tr>
<tr>
<td>Coulombic efficiency ((\eta)) %</td>
<td></td>
<td>96</td>
<td>90.</td>
<td>94</td>
</tr>
</tbody>
</table>
4.2.6 Electrochemical Impedance Spectroscopy (EIS) Study

In order to investigate the electrochemical behavior at the electrode/electrolyte interface in detail, electrochemical impedance spectroscopy (EIS) measurement was carried over the frequency range from 0.01 to $10^5$ Hz. Fig. 4.18 shows the electrochemical impedance spectra in the form of Nyquist plane plots for (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin films. All the impedance plots show a semicircle in the high frequency region due to the charge-transfer resistance and a $45^\circ$ capacitive slope in the low frequency region. The high frequency intercept of the semicircle on the real axis provides the value of ohmic resistance, which include the resistance of an electrolyte, the intrinsic resistance of the active material, and the contact resistance at the interface active material/current collector. The diameter of the semicircle gives an approximate value of the ESR at the electrodes/electrolyte interface. From Fig. 4.18, the observed ESR for RuO$_2$, PANI-RuO$_2$ composite and PANI electrodes were 6, 60 and 11 Ω, respectively [46].

**Fig.4.17:** Galvanostatic charge-discharge curves of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (C) PANI thin film electrodes.
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**Fig. 4.18:** Nyquist plots of (a) RuO$_2$, (b) PANI-RuO$_2$ composite, and (c) PANI thin film electrodes.

**4.B.2.7 Conclusions**

The SILAR deposited PANI-RuO$_2$ composite electrode showed the maximum specific capacitance of 664 F.g$^{-1}$ at the scan rate of 5 mV.s$^{-1}$. The stability of the PANI-RuO$_2$ composite electrode showed 89% stability over the 5000$^{th}$ cycles. Though the PANI-RuO$_2$ composite shows the less specific capacitance as compared with PANI specific capacitance of 1078 F.g$^{-1}$, we have observed greater/improved stability than the PANI electrode. Thus, composite film would stay for better cycle life as compared to the pure RuO$_2$ and PANI. The lower specific capacitance of PANI-RuO$_2$ composite electrode may be due to the larger internal resistance revealed from the electrochemical impedance analysis. The specific power and specific energy of the PANI-RuO$_2$ composite electrode were found to be 3.57 KW.kg$^{-1}$ and 432 Wh.kg$^{-1}$, respectively. The 90% coulombic efficiency was observed from the charge-discharge study of the PANI-RuO$_2$ composite electrode.
Section C

NH₃ Gas Sensor Properties of PANI–RuO₂ Composite Thin Films

4.C.1 Introduction

The ammonia sensors have vital role in the area of process control, environmental analysis, leak detection in compressor rooms of air conducting, and breath analysis for medical diagnoses. Sensors based on inorganic semiconductors operate at high temperatures, which increase cost and complexity of the devices. On the other hand, sensors based on organic materials can be operated at room temperature [47, 48].

4.C.2 Ammonia Sensing Properties of PANI–RuO₂ Composite Thin Films

The mechanism of ammonia sensing is described in section 3.C.3

4.C.3 Effect of Film Thickness

Fig. 4.19 shows the NH₃ gas response as a function of different thickness under the exposure of 20 ppm NH₃ gas at 300 K for PANI-RuO₂ composite thin film. PANI-RuO₂ composite thin film showed gas response at room temperature. Further, it can be evidenced from the figure that the sensitivity increases with increase in thickness of sensor element. The 18% sensitivity was observed at low thickness which was increased up to the 40% for the highest thickness of 0.11 mg.cm⁻² on the exposure of 20 ppm NH₃ gas concentration at 300 K. It is well known that the sensitivity of the metal oxide semiconductor sensors is mainly determined by the interaction between the target gas and the surface of the sensors. So it is obvious that for the greater surface area of the materials, the interaction between the adsorbed gases and the sensor surface are stronger, i.e. gas sensitivity is higher [49]. On the other hand, the sensor is based on polymer-metal oxide and hence the long polymer chain may provide a large surface giving the significant effect on increase in sensitivity with increase in sensor thickness.
Fig. 4.19: The thickness dependent gas response of PANI-RuO$_2$ composite thin to 20 ppm NH$_3$ gas concentration at 300 K.

4.C.4 Effect of Gas Concentration

The resistance curves of PANI-RuO$_2$ composite thin film thickness of 0.11 mg.cm$^{-2}$ at 300 K on the exposure of different concentrations of NH$_3$ gas are shown in Fig. 4.20. The PANI-RuO$_2$ composite sensor element shows the quick response to the resistance as soon as the NH$_3$ gas is entered in the gas chamber and fast recovery, when the chamber is evacuated. Thus the PANI-RuO$_2$ composite thin film shows the fast response and recovery for all the gas concentrations. The PANI-RuO$_2$ composite sensor was tested for the NH$_3$ gas concentration ranging from 20 to 100 ppm. It is observed that when the concentration is increased from 20 to 80 ppm, the resistance increases showing the increase in sensitivity from 40% to 79%. The gas response of a sensor depends on the reaction between target gas and exposed area of the sensor. For a low concentration (20 ppm) of NH$_3$ gas exposed on a fixed surface area of sample, there is a lower coverage of NH$_3$ gas molecule on surface and hence lower surface reaction occurred. An increase in NH$_3$ gas concentration increases the surface reaction due to the larger surface coverage of NH$_3$ gas molecules, resulting in increase in gas response. Thus, for PANI-RuO$_2$ composite thin film the maximum gas response of 79% was observed on the
exposure of 80 ppm NH₃. After the 80 ppm of the NH₃ gas concentration, the gas response decreases. The PANI-RuO₂ composite shows the 102 s response time and 122 recovery time. Fig. 4.21 shows the gas response of the (a) PANI and (b) PANI-RuO₂ composite thin film sensors on the exposure of different concentrations of NH₃ gas. From Fig. 4.21, it is observed that PANI-RuO₂ composite sensor shows the greater gas response than the PANI sensor gas response of 59%.

\[ \text{Fig. 4.20: Resistance response curves of PANI-RuO}_2 \text{ composite thin film to different NH}_3 \text{ gas concentrations at 300 K.} \]
4.C.5 Selectivity Study

The ability of a sensor to respond to a certain gas in the presence of other gases is known as selectivity. Selectivity of PANI-RuO$_2$ composite thin film was studied under the exposure of different gases CO$_2$, N$_2$, NH$_3$ and LPG at room temperature is shown in Fig. 4.22. The PANI-RuO$_2$ composite thin film showed more selectivity towards NH$_3$ at 20 ppm as compared to CO$_2$, N$_2$, and LPG gas. This may be due to the correlation with the interaction strength between the testing gas and sensing layer [50].

**Fig. 4.21:** The gas response of (a) PANI and (b) PANI-RuO$_2$ composite thin films to different NH$_3$ gas concentration.
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Fig. 4.22: Comparative gas responses of PANI-RuO$_2$ composite thin film to different gases at 300 K.

4.C.6 Conclusions

The NH$_3$ sensing properties of the PANI-RuO$_2$ composite were film thickness dependent. The maximum response of 79 % at 300 K was found under the exposure of 80 ppm of NH$_3$ for 0.11 mg.cm$^{-2}$ thickness. It is observed that the PANI thin film shows lower response than the PANI-RuO$_2$ composite thin films. The higher response of PANI-RuO$_2$ composite sensor is attributed to the formation of p-n junction in composite material. The PANI-RuO$_2$ composite thin films exhibited good gas response time 102 s and recovery time 122 s.
## References

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>References</th>
</tr>
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</table>
1925.


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