### CHAPTER-V

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5.1 Introduction

The performance of supercapacitor electrode strongly depends upon the active materials involved, their reversible redox transitions between various oxidation states and morphology [1]. The morphology of the supercapacitor electrode is an important aspect, as it is well known that the porous morphology of the electrode is useful for supercapacitor application because such morphology provides higher effective surface area. The morphology and hence the supercapacitive performance of electrode can be tuned by various surface treatments. In earlier studies, specific capacitance of ruthenium oxide has been enhanced by surface treatments like annealing in air [2, 3] electrochemical anodization in aqueous media [4] and ultrasonic wordering in NaOH [5].

In the present work, tin oxide ruthenium oxide (SnO$_2$-RuO$_2$) composite electrodes prepared by SILAR and CBD methods are treated by various surface treatments such as annealing in air, ultrasonic wordering in NaOH and anodization. The effect of these surface treatments on the morphology, wettability and specific capacitance of the SnO$_2$-RuO$_2$ composite film is studied.

5.2 Experimental Details

The optimized SnO$_2$-RuO$_2$ composite films showing maximum specific capacitance value were prepared by SILAR (SnO$_2$:RuO$_2$= 1:3, sample S3) and CBD (15 vol%, sample C3) methods as described in earlier sections. The deposition was taken on large area stainless steel (> 16 cm$^2$) substrates. The thickness of the deposited film is measured by method described in section 3.A.3.2. The substrate is then cut into 4 identical substrates of ~ 4 cm$^2$ area and used for surface treatment study. For air annealing, SnO$_2$-RuO$_2$ composite electrode was annealed in air at 423 K for 2 h. For ultrasonic wordering, the substrate coated with SnO$_2$-RuO$_2$ was ultrasonically wordering in 1 M NaOH for 30 min in ultrasonic cleaner and
the anodization treatment was carried out in 0.1 M H₂SO₄ at +1.2 V for 1.30 h using potentiostat/ Galvanostat. It was observed that the SnO₂-RuO₂ composite film prepared by SILAR is unstable in NaOH solution so that the ultrasonic wetering was not done for SILAR deposited SnO₂-RuO₂ composite film.

5.3 Results and Discussion

5.3.1 Effect of Surface Treatments on SnO₂-RuO₂ Composite Film Prepared by SILAR Method

5.3.1.1 Effect of Air Annealing

The morphology of pristine and air annealed SnO₂-RuO₂ composite film prepared by SILAR method is shown in Fig. 5.1 (a, b). The pristine SnO₂-RuO₂ composite film surface contains porous irregular shaped agglomerated morphology, which changed to a granular and comparatively smooth surface with overgrowth of particles after air annealing. The contact angle image for pristine and air annealed SnO₂-RuO₂ composite film is shown in Fig. 5.2 (a, b). The contact angle for pristine SnO₂-RuO₂ composite film is 121° changed to 13° for annealed SnO₂-RuO₂ composite film, which shows the hydrophobic nature of the composite film is changed to hydrophilic after air annealing. It was observed that the surfaces with high surface energy are hydrophilic. As with air annealing, there is possibility of formation of nanocrystalline structure for SnO₂-RuO₂ composite, the nanocrystalline surface has greater surface energy, resulting in the decrease in water contact angle [6].

The supercapacitive performance of annealed SnO₂-RuO₂ composite electrode is studied using cyclic voltammetry (CV) in 0.5 M H₂SO₄ electrolyte at 5 mV.s⁻¹ scan rate in the potential range of -0.2 to +0.6 V vs. SCE. The cyclic voltammogram (Fig. 5.3) showed that specific capacitance is decreased from 183 to 67 F.g⁻¹ for annealed SnO₂-RuO₂ composite electrode compared with pristine electrode. The loss in specific
capacitance value is due to the a significant loss in the water content resulting in a more ordered structure which render a higher barrier for proton diffusion in comparison with their pristine structure [7]. Also there may be formation of nanocrystalline structure with decrease in defects (i.e. electroactive sites), decreasing the specific capacitance of electroactive species [5].

**Fig. 5.1:** The morphology of (a) pristine and (b) after air annealing for SnO$_2$-RuO$_2$ composite film (sample S3).

**Fig. 5.2:** The water contact angle images of (a) pristine and (b) after air annealing for SnO$_2$-RuO$_2$ composite film (sample S3).
5.3.1.2 Effect of Anodization

The effect of anodization on the morphology and wettability of SnO$_2$-RuO$_2$ composite film is studied. Fig. 5.4 (a) shows the morphology of SnO$_2$-RuO$_2$ composite film after anodization treatment. The spongy and porous morphology is observed for SnO$_2$-RuO$_2$ composite film after anodization. The water contact angle decreased to 72$^\circ$ compared with pristine SnO$_2$-RuO$_2$ composite film as observed from Fig. 5.4 (b).

The CV curve for anodized SnO$_2$-RuO$_2$ composite electrode is shown in Fig. 5.5. From the CV curve, decrease in voltammetric current is observed for anodized SnO$_2$-RuO$_2$ composite electrode. The specific
capacitance decreased from 183 to 106 F.g\(^{-1}\) for anodized SnO\(_2\)-RuO\(_2\) composite electrode compared with pristine composite electrode.

**Fig. 5.4:** (a) The morphology and (b) water contact angle image of anodized SnO\(_2\)-RuO\(_2\) composite film (sample S3).
Fig. 5.5: The CV curves for pristine and anodized SnO$_2$-RuO$_2$ composite electrode in 0.5 M H$_2$SO$_4$ electrolyte at 5 mV.s$^{-1}$ between -0.2 to +0.6 V vs. SCE.

The comparative study of surface treatments on the contact angle and specific capacitance value of SnO$_2$–RuO$_2$ composite is shown in table 5.1.
Table 5.1

Effect of surface treatments on specific capacitance value of SILAR deposited SnO$_2$-RuO$_2$ composite electrode.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Surface treatment</th>
<th>Sample Area (cm$^2$)</th>
<th>Contact Angle (°)</th>
<th>Specific Capacitance (F.g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pristine</td>
<td>1</td>
<td>121</td>
<td>183</td>
</tr>
<tr>
<td>2.</td>
<td>Air annealing (423 K, 2 h)</td>
<td>1</td>
<td>13</td>
<td>67</td>
</tr>
<tr>
<td>3.</td>
<td>Anodization (0.1M H$_2$SO$_4$ at +1.2 V vs. SCE for 1.30 h)</td>
<td>1</td>
<td>72</td>
<td>106</td>
</tr>
</tbody>
</table>

5.3.2 Effect of Surface Treatment on SnO$_2$-RuO$_2$ Composite Film prepared by CBD Method

5.3.2.1 Effect of Air Annealing

In general, hydrous ruthenium oxide annealed in the temperature region close to its crystallization temperature showed a very high specific capacitance (≥720 F.g$^{-1}$) [2]. This has been attributed to the local structures of hydrous ruthenium oxide retaining facile transport pathways for both protons and electrons [8]. The SEM images for pristine and air annealed SnO$_2$-RuO$_2$ composite films are shown in Fig. 5.6 (a) and water contact angle image for pristine SnO$_2$-RuO$_2$ composite film prepared by CBD method are shown in Fig. 5.6 (a, b). The morphology of annealed SnO$_2$-RuO$_2$ composite film and corresponding water contact angle are shown in Fig. 5.7 (a, b). The larger pits observed in case of pristine SnO$_2$-RuO$_2$ composite electrode are vanished in annealed electrode. There is no much difference in water contact angle of pristine and annealed SnO$_2$-RuO$_2$ composite electrode. The CV curve for pristine and annealed SnO$_2$-
RuO$_2$ composite electrode (sample C3) in the potential range of 0 to +0.8 V vs. SCE at 20 mV.s$^{-1}$ in 0.5 M H$_2$SO$_4$ electrolyte is shown in Fig. 5.8. The current was reduced significantly for annealed composite electrode reducing its specific capacitance value from 166 to 12 F.g$^{-1}$. The significant decrease in specific capacitance value after annealing is attributed to the loss of hydrous content from the sample [9].

**Fig. 5.5:** The morphologies of (a) pristine and (b) after air annealing for SnO$_2$-RuO$_2$ composite film (sample C3).

**Fig. 5.6:** The water contact angle images of (a) pristine and (b) after air annealing for SnO$_2$-RuO$_2$ composite film (sample C3).
Fig. 5.8: The CV curves for pristine and annealed SnO$_2$-RuO$_2$ composite electrode (sample C3) in 0.5 M H$_2$SO$_4$ electrolyte at 20 mV.s$^{-1}$ between 0 to +0.8 V vs. SCE.

5.3.2.2 Effect of Ultrasonic Weltering

The effect of ultrasonic weltering in NaOH on SnO$_2$-RuO$_2$ composite electrode is studied. Fig. 5.9 (a, b) shows the surface morphology and water contact angle image for ultrasonically weltered SnO$_2$-RuO$_2$ composite electrode respectively. The bigger pits and elongated structure observed for pristine SnO$_2$-RuO$_2$ composite (Fig. 5.6 a) is vanished for ultrasonically weltered composite electrode with small pits distributed all over the surface. The water contact angle for ultrasonically weltered SnO$_2$-RuO$_2$ composite film is not much altered with slight decrease compared with pristine composite film.
Fig. 5.10 shows the CV curves for pristine and ultrasonically weltered SnO$_2$-RuO$_2$ composite electrode. The specific capacitance value is decreased from 166 to 106 F.g$^{-1}$ for ultrasonically weltered SnO$_2$-RuO$_2$ composite electrode compared with pristine electrode. This means the ultrasonic weltering treatment is not suitable for SnO$_2$-RuO$_2$ composite electrode as decrease in specific capacitance value was observed. Slight loss in weight of deposited film was observed after ultrasonic treatment due to the removal of unbound surface particles.

**Fig. 5.9:** (a) The morphology and (b) water contact angle image of ultrasonically weltered SnO$_2$-RuO$_2$ composite film (sample C3).
Fig. 5.10: The CV curves for pristine and ultrasonically weltered SnO$_2$-RuO$_2$ composite electrode in 0.5 M H$_2$SO$_4$ electrolyte at 20 mV.s$^{-1}$ between 0 to +0.8 V vs. SCE.

5.3.2.2 Effect of Anodization

The effect of anodization on SnO$_2$-RuO$_2$ composite electrode is studied. Fig. 5.11 (a, b) shows the morphology and contact angle image for SnO$_2$-RuO$_2$ composite electrode after anodization. The morphology of the electrode is changed from rough with irregular pits and elongated structure to relatively smooth surface covered all over the substrate after the anodization. The hydrophilic surface of pristine SnO$_2$-RuO$_2$ composite electrode was changed to superhydrophilic with water contact angle $\sim$70$^\circ$.

The CV curve for pristine and anodized SnO$_2$-RuO$_2$ electrode is shown in Fig. 5.12. From which it is observed that there is a increase in current response for SnO$_2$-RuO$_2$ electrode after anodization. There is
possibility of presence of some chloride precursors in pristine samples, with anodization there is formation of impurity free SnO$_2$-RuO$_2$, which improves the conductivity. Also as the surface is smooth and porous the electrolyte can easily access the bulk of the electrode, which results into maximum current response. [4]. Thus, anodization method is found to be useful surface treatment for SnO$_2$-RuO$_2$ composite electrode prepared by CBD method.

Fig. 5.11: (a) The morphology and (b) water contact angle image of anodized SnO$_2$-RuO$_2$ composite film (sample C3).
Fig. 5.12: The CV curves for pristine and anodized SnO$_2$-RuO$_2$ composite electrode (sample C3) in 0.5 M H$_2$SO$_4$ electrolyte at 20 mV.s$^{-1}$ between 0 to +0.8 V vs. SCE.

The comparative study of surface treatments on the contact angle and specific capacitance value of SnO$_2$–RuO$_2$ composite is shown in Table 5.2.
Table 5.2

Effect of surface treatments on specific capacitance value of CBD deposited SnO$_2$-RuO$_2$ composite electrode.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Surface Treatment</th>
<th>Sample Area (cm$^2$)</th>
<th>Contact Angle ($^\circ$)</th>
<th>Specific Capacitance (F.g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pristine</td>
<td>1</td>
<td>14</td>
<td>166</td>
</tr>
<tr>
<td>2</td>
<td>Air annealing (423 K, 2 h)</td>
<td>1</td>
<td>13</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>Ultrasonic weltering (in 1 M NaOH for 30 min)</td>
<td>1</td>
<td>12</td>
<td>106</td>
</tr>
<tr>
<td>4</td>
<td>Anodization (0.1 M H$_2$SO$_4$ at +1.2 V vs. SCE for 1.30 h)</td>
<td>1</td>
<td>7</td>
<td>269</td>
</tr>
</tbody>
</table>

Conclusions

The effect of surface treatments on the morphology, wettability and specific capacitance on SnO$_2$-RuO$_2$ composite films deposited by SILAR and CBD method is studied successfully. It is observed that the morphology of the SnO$_2$-RuO$_2$ composite film deposited by SILAR method changed with annealing and anodization, in addition the hydrophobic surface of pristine composite film changed to hydrophilic. The specific capacitance value decreased for both annealed and anodized SnO$_2$-RuO$_2$ composite electrode deposited by SILAR method. In case of SnO$_2$-RuO$_2$ composite films deposited by CBD method the surface treatments changed the morphology to relatively smooth surface. The decrease in specific capacitance is observed for annealed and ultrasonically weltered SnO$_2$-RuO$_2$ composite films deposited by CBD method. However, with anodization treatment the
specific capacitance of the composite electrode deposited by CBD method is increased compared with pristine composite. This may be due the enhancement in conductivity of SnO$_2$-RuO$_2$ after anodization.
CHAPTER-V: EFFECT OF SURFACE TREATMENTS ON MORPHOLOGY, WETTABILITY AND SPECIFIC CAPACITANCE OF TIN OXIDE RUTHENIUM OXIDE COMPOSITE THIN FILMS

References


