This Chapter describes methods and techniques applied for synthesis of SnO₂ compact layer over FTO substrate. The first part deals with introduction, preparation of SnO₂ compact layer of different thicknesses for device fabrication and their characterization. The second part of the chapter gives detailed description for preparation of porous layer with different thicknesses and their characterization. The third part describes observed experimental results and discussions over effect of compact layer thickness, porous layer thickness on performance of DSSC.
4.1: Introduction

In DSSC, under the illumination, dye molecules are excited and photoelectrons are produced. These electrons pass through four important interfaces: dye/semiconductor, semiconductor/fluorine doped tin oxide (FTO), dye/electrolyte and electrolyte/counter electrode. Unidirectional flow of generated charges with no loss at these interfaces is very critical for high photoconversion efficiency of DSSCs [1, 2]. As described earlier (performance limiting processes), the injected electrons from dye to metal oxide semiconductor can undergo recombination [3-5]:

i. With the oxidized sensitizer itself.

ii. With the redox mediator at the metal oxide/electrolyte interface.

iii. With the redox mediator at the FTO/electrolyte interface, as the electrolyte is in contact with FTO through the mesoporous photovoltaic film.

Among these interfaces, one of the losses due to recombination of electrons occurs at the interface of semiconductor/FTO because of direct contact of electrolyte with FTO [6-8]. These recombination losses generally contribute to decreasing the shunt resistance of the solar cells thus affecting its photovoltaic performance. The decrease in shunt resistance takes place due to number of processes, including recombination of conduction band electron with the oxidized dye and redox electrolyte species at photovoltaic/dye and photovoltaic/FTO interface [8-10]. The mesoporous structure of photovoltaic, which is necessary for sufficient dye loading, allows the electrolyte to penetrate towards the FTO, leading to decreased shunt resistance [11]. To prevent recombination of electrons at FTO with the oxidized species of electrolyte, a thin compact layer (CL, usually known as blocking layer) can be formed between the mesoporous oxide and FTO substrate. The blocking layer prevents direct physical contact between the FTO and the electrolyte, and has been reported to lead to an increase in the overall conversion efficiency of the cell [12].

The schematic on the effect of the blocking layer is shown in Fig. 4.1. In this modified structure of the device, the FTO serves as a conducting electrode which is also transparent to allow the light to reach dye/photovoltaic junctions. The next
Influence of Geometrical Thickness of Compact/Porous SnO$_2$ Photoanode Films on the Performance of Dye Sensitized Solar Cells

Layer, compact metal oxide film acts as blocking layer to prevent the electrolyte from reaching the FTO substrate. Over this porous layer of SnO$_2$ nanoparticles is formed, which provides high surface area as compared to a flat surface and enables sufficient dye loading for maximum light harvesting.

![Fig. 4.1: Schematic of DSSC (A) without compact layer; (B) with compact layer.](image)

Previous investigations on TiO$_2$ based DSSCs, the incorporation of compact TiO$_2$ thin layer between FTO and mesoporous TiO$_2$ film showed enhancement of performance of the device by two to three orders of magnitude [3,7,13,14]. In addition to TiO$_2$, ZnO, Nb$_2$O$_5$ and MgO, Al$_2$O$_3$, SiO$_2$, SnO$_2$, Eu$_2$O$_3$, CaCO$_3$ and BaCO$_3$, have also been used as a blocking layer for the fabrication of DSSCs [2, 11, 15-20]. It is worth mentioning here that no study especially on SnO$_2$ compact layer for SnO$_2$ based DSSC is found in the literature.

It has been observed that different methods have been employed for the preparation of compact films viz. chemical vapor deposition, radio-frequency and direct-current (DC) sputtering, spray pyrolysis, dip coating and spin coating etc. [3,7,14,21]. Kavan and Grätzel have reported synthesis of a compact TiO$_2$ layer obtained by aerosol pyrolysis technique for DSSC application [22]. The physical methods for film deposition require high vacuum systems, purity of metal and are energy intensive. Also the produced films are weakly bounded to the substrate [4]. On the other hand, a chemical route, especially sol gel with either dip or spin coating does not require highly precise equipment and expensive chemicals. Also the film can be deposited at low temperature as compared to other processes [8,14]. However, the control over solution viscosity, substrate cleaning, deposition parameters are necessary to obtain good quality of film. Moreover, thick compact layer on FTO may
increase series resistance, thus can interrupt the injection of electrons from the porous photoelectrode to conducting substrate [7,12,23]. Therefore, the photovoltaic characteristic of DSSC can further improve by optimizing CL thickness and thus reduces the charge transfer resistance.

With this, the optimal Dye loading and light harvesting capability of photoanode are two important aspects which can be influenced by the design of the photoelectrode [24-26]. Geometrical thickness of the photoanode film does profoundly affect these two aspects related to DSSC [24, 25]. Dye loading in the electrode depends on the porous nature of the film and porosity is a function of the thickness of the photoanode film. Subsequently, scattering of light in photoanode, results in the increase of path length of light inside the film, thus leading to its improved light harvesting ability [27]. However, the light scattering magnitudes do also depend on the thickness of the film [24, 28]. For the photoanodes prepared from the same paste, the optical thickness of the film solely is a function of the geometrical thickness of the photoanode. In view of the above, it is imperative to study the effect of geometrical thickness of the photoanode on the performance of the cell.

In the light of the above, the present work had been planned and executed systematically with three main objectives: i) study the effect of introducing compact SnO$_2$ layer coated FTO as blocking layer on performance of SnO$_2$ based DSSC. ii) analyze the effect of geometrical thickness of the photoanode on the performance of the SnO$_2$ based DSSC and iii) the optimized compact layer is incorporated with photoanodes with different thicknesses and the performance has been studied.

4.2: Experimental details

4.2.1: Materials

SnCl$_2$2H$_2$O and hydrochloric acid (HCl) were purchased form THOMAS BAKER for the preparation of SnO$_2$ sol for the preparation of compact films. For photoanode porous layer preparation the SnO$_2$ paste was prepared as per the procedure described in chapter-3. Eosin-Y (2-(2, 4, 5, 7-tetramethoxo-3-oxo-3H-xanthene-9-yl) benzoate, C$_{20}$H$_{16}$Br$_4$Na$_2$O$_5$) dye was purchased from HIMEDIA. FTO glass substrates were pre-cleaned ultrasonically in distilled water, acetone and alcohol each as per the procedure given in section 2.4.
4.2-2: Compact layer preparation

The substrate, of FTO was cut to a size of 2.5 X 2.5 cm and used for the cell preparation. A tape mask, with a 1.5 × 2.5 cm open area for photoelectrode deposition, was placed on the FTO-coated substrate. To prepare compact SnO₂ films, precursor solution of 0.1M SnCl₂2H₂O in methanol solvent was prepared under vigorous stirring. After addition of SnCl₂2H₂O, few drops of concentrated HCl were added to render the transparent solution. The solution was kept on constant stirring for 1 h. The CL of SnO₂ was prepared using spin coater. The FTO was kept on the rotating disk of the coater, and then few drops of the prepared sol were dropped onto it. The deposition was carried out at 3000 rpm for 30 seconds at an acceleration of 200 in order to evenly distribute the sol. To get uniform compact film, the methanol solution containing SnCl₂2H₂O precursor must spread evenly on an FTO substrate. To get crack and pin-hole free films the processing parameters and viscosity of the solution have to be optimized. After deposition of one layer, the film was dried at 90°C for 30 min. The films with three different thicknesses were prepared by repeating above process numerous times. Accordingly the samples known as CL-1, CL-2, and CL-3. All the samples were annealed at 250°C in air for 2 hr.

4.2-3: Preparation of SnO₂ compact–porous layer films

The paste of SnO₂ nanoparticle was prepared as per the procedure defined in of Chapter-3 sections 3.2. The SnO₂ photoelectrodes were prepared concurrently according to the same procedure on the CL-FTO and FTO substrates by screen-printing technique. A substrate was fixed on the screen-printing setup and SnO₂ paste was swept over a sieve (mesh size 90 m) with a plastic squeeze block. After removing the sieve, a film of porous SnO₂ paste was formed on the substrate. The photoelectrodes were subjected to the sintering process at temperature, 450°C for 30 min. The porous-SnO₂ layer thickness after sintering was around 1μm. The photoanodes with different compact layer were named as P-CL1, P-CL2 and P-CL-3.

4.2-4: Preparation of SnO₂ porous layer films of different thicknesses

In this work the SnO₂ photoanodes of five different thicknesses were fabricated using doctor blading and screen printing methods over FTO conducting substrate and are named PA1 to PA5 in the order of increasing thickness.
4.2-5: DSSC fabrication

Dye sensitization was carried out by immersing all the prepared photoelectrodes in 0.3 mM Eosin-Y solution in ethanol for about 24 hours. DSSCs were fabricated using FTO/Compact SnO\textsubscript{2} (CL)/ porous SnO\textsubscript{2} (PL) / EY as a photoanode and Pt coated FTO as a counter electrode. Few drops of electrolyte solution were added onto EY/SnO\textsubscript{2} photoanode before clamping it with the Pt-coated FTO counter electrode.

4.3: Characterization

Profilometery (KLA Tencor P\textsubscript{16+}) was used to determine thickness of the photoelectrode films. Transmittance, diffuse reflectance and optical absorption spectroscopic studies were conducted for both unsensitized and dye sensitized photoanode films using JascoV-670 spectrometer. The surface morphologies of the films were studied by a scanning electron microscopy (SEM, JEOL-JSM 6360-A). To evaluate the effect of compact layer and photoanode thickness on performance of DSSC, the devices were fabricated using P-CL\textsubscript{1} to P-CL\textsubscript{3} and PA1 to PA5 films by making use of poly-iodide as electrolyte and platinized FTO coated substrate as the counter electrode. All the cells were tested under AM 1.5 solar simulator equipped with a 450W xenon lamp at 100 mW/cm\textsuperscript{2} (Model Sol 2A, Newport) for studying photovoltaic performance of these optoelectronic devices.

4.4: Results and Discussion

4.4-1: SnO\textsubscript{2} compact layer films

4.4-1(i): Surface morphological analysis

The observed surface SEM micrographs of compact SnO\textsubscript{2} layer deposited FTO substrate has been shown in Fig. 4.2. All the CLs cover the rough FTO substrate completely and are observed to be homogeneous and do not contain holes and cracks. Thus, these films can successfully avoid the contact of electrolyte with FTO substrate.

4.4-1(ii): Film thickness measurement

The thickness of resultant films was obtained by using the KLA Tencor P\textsubscript{16+} surface profilometer. For the measurement of thickness of given film, the stylus is allowed to scan a surface from uncovered part of substrate to few portion of the film.
The thickness of photoanode CL-1, CL-2 and CL-3 is found to be 75, 140, 370 nm, respectively.

Fig. 4.2: SEM micrographs of Porous SnO$_2$ layer and Compact SnO$_2$ layer of different thicknesses.

Fig. 4.3: Variation of contact angle with compact layer thickness.

4.4-1(iii): Contact angle measurement

The wettability of CLs of SnO$_2$ films prepared on FTO substrate was investigated by contact angle method. The variation of contact angle on the film
surface with different compact layer thickness is shown in Fig. 4.3. The CL showed value of contact angle decreases with increase in film thickness. This shows that SnO$_2$ films grows hydrophilic with increase in film thickness.

4.4-1(iv): Optical properties of SnO$_2$ compact film

The Transmittance and absorbance spectra of CL SnO$_2$ films annealed at 250$^\circ$C in the wavelength region from 200 to 800 nm are shown in Fig. 4.4. The transmittance spectrum of the coatings reveals that the transmittance of the films is about 85 to 90 % in this visible region. As expected the transmission of the CLs decreases with increasing thickness from CL-1 to CL-3. The lowering of transmission for the CL-3 may be due to thickness and scattering by the grain boundaries. From Fig. 4.4(inset) of absorption spectra of CLs, the strong absorption at about 290 nm is observed. From figure it is observed that, he absorption increases with increasing the film thickness.

![Fig. 4.4: Transmittance spectra for Compact SnO$_2$ layer of different thicknesses
Inset: Absorption spectra for Compact SnO$_2$ layer of different thicknesses)](image)

4.4-2: Optical properties of un-sensitized and EY-sensitized SnO$_2$ compact - porous films

The comparative absorption spectra for the photoanode with and without compact layer and the CLs are shown in Fig. 4.5. It is clearly seen that the absorption
of porous layer is much higher than that of CLs, while no considerable change in absorbance is observed in the absorbance of porous layer after introduction of CLs.

![Absorption spectra for Compact SnO₂ layers and compact-porous SnO₂ photoelectrode](image1)

**Fig. 4.5**: Absorption spectra for Compact SnO₂ layers and compact-porous SnO₂ photoelectrode

![Absorption spectra of un-sensitized and sensitized Porous; compact-porous SnO₂ photoelectrode with different compact layers](image2)

**Fig. 4.6**: Absorption spectra of un-sensitized and sensitized Porous; compact-porous SnO₂ photoelectrode with different compact layers.

**Fig. 4.6** shows the optical absorption spectra of bare SnO₂ and Eosin-Y sensitized SnO₂ photoanode with different CLs. It is observed that the absorption of SnO₂ is limited only to ultraviolet light region, whereas for Eosin–SnO₂, it is extended...
to visible region about 550 nm. For the photoanode with increasing thickness of CLs, an increased absorbance at about 550 nm is observed.

**4.4-3: Characterization of un-sensitized and EY-sensitized SnO$_2$ porous films: effect of geometrical thickness**

Increasing the thickness of the porous photoanode increases the surface area of the photoanode film. This is believed to facilitate more dye loading in the thicker films. In the present study, the dye residence time is kept constant for all the films. The light harvesting efficiency ($LHE$) of the photoanode film can be improved either by increasing the dye concentration or increasing the amount of light scattering in the film leading to increased path length of incident light inside the photoanode. The contribution of the former vis-à-vis latter is negligible in the present investigation, since optimal dye loading cannot be assumed in all the films by virtue of constant dye residence time that was maintained for all of them. As claimed in the literature, optimal dye loading durations are different for different thicknesses of the photoanode films [25]. As described above, the $LHE$ can also be improved by increasing the path length of the light radiation which actually depends on the light scattering in the films. Thus in the present study, the effect of thickness over the $LHE$ is given emphasis by taking light scattering in the films into consideration.

**4.4-3(i): Film thickness measurement**

The thickness of resultant films was obtained by using the KLA Tencor P$_{16+}$ surface profilometer. For the measurement of thickness of given film, the stylus is allowed to scan a surface from uncovered part of substrate to few portion of the film. It provides a step necessary for the measurement of film thickness. The thickness of photoanode PA1, PA2, PA3, PA4 and PA5 is found to be 1, 3, 6, 8 and 14 µm, respectively.

**4.4-3(ii): Reflectance spectra of bare SnO$_2$ porous films: effect of geometrical thickness**

Diffused reflectance spectroscopy of the photoanode films is one of the techniques that are generally used to measure the magnitudes of light scattering [28]. Greater the diffused reflectance from a film, better the light scattering ability of the film which may lead to improved light harvesting. The reflectance spectra of the films
PA1 to PA5 are presented in Fig. 4.7. It clearly shows that the light scattering magnitudes have considerably increased with thickness especially, in the visible range. Thus, the film with highest thickness is expected to give better performance by virtue of enhanced path length of light, probably resulting in better light harvesting in it.

![Diffused reflectance spectra of PA1 to PA5 films of different thicknesses.](image)

**Fig. 4.7:** Diffused reflectance spectra of PA1 to PA5 films of different thicknesses.

4.4.3(iii): *Absorption spectra of un-sensitized and EY-sensitized SnO$_2$ porous films: effect of geometrical thickness*

The photoanode films were subsequently sensitized with Eosin-Y dye. **Fig. 4.8** shows the absorbance spectra of these films. The absorption spectra show enhanced absorbance in the dye absorption region with increasing thickness. This supports the above proposition of enhanced absorbance due to better *LHE* as a result of increased scattering magnitudes from PA1 to PA5.

**Fig. 4.9** shows the absorbance spectra of PA1 to PA4 photoanodes with and without compact layer. The absorption spectra in the dye absorption region do not vary considerably for the photoanodes with CL.
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Fig. 4.8: Absorption spectra of dye loaded photoelectrodes from PA1 to PA5. (Inset: Absorption spectrum of solution containing 0.3 mM Eosin-Y dye in ethanol)

Fig. 4.9: Absorption spectra of dye loaded photoelectrodes with optimized compact layer CL-2 with PA1 to PA5 in dye region.
4.5: Solar cell characterization

4.5-1: DSSC based on EY- Sensitized SnO₂ compact – porous photoanode films: effect of compact layer thickness

Fig. 4.10 gives the photocurrent density (J) - voltage (V) curves of the four DSSCs fabricated with the FTO/porous SnO₂, FTO/ CL-1/ porous SnO₂ / FTO/ CL-2/ porous SnO₂ / FTO/ CL-3/ porous SnO₂, respectively. The photovoltaic parameters are summarized in Table 4.1.

![Graph showing J-V characteristics for solar cells](image1)

Fig. 4.10: Current density Vs voltage (J-V) characteristics for solar cells constructed using Eosin-Y sensitized photoanodes with CLs of different thicknesses

![Graph showing variation of Voc and Jsc](image2)

Fig. 4.11: Variation of Voc and Jsc for DSSCs based on photoanodes with CLs of different thicknesses.
Fig. 4.11 shows the variation of short-circuit photocurrent density ($J_{SC}$), open-circuit voltage ($V_{OC}$) with different photoanodes with CL. It has been observed that the PCE of the DSSC fabricated with CL-2 of thickness 140 nm is higher than that of the DSSC fabricated with CL-1 and CL-3 of thicknesses 75 and 370 nm, respectively. The value of $J_{SC}$ increases from 0.39 to 1 mA/cm$^2$ after incorporation of CL-2 in between FTO and porous SnO$_2$, and also decreased with further increase in CL thickness.

The $V_{OC}$ also slightly improved by addition of compact layer. The $V_{OC}$ of 0.29 V is enhanced to approximately 0.35 V after incorporation of CL-2 with thickness 140 nm. As a result, the overall conversion efficiency increases from 0.06 % without CL to 0.19 % with CL-2.

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>Thickness of CL (nm)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>1 $\mu$m</td>
<td>0.29</td>
<td>0.39</td>
<td>51.03</td>
<td>0.06</td>
</tr>
<tr>
<td>CL-1/P</td>
<td>75</td>
<td>0.32</td>
<td>0.52</td>
<td>51.03</td>
<td>0.09</td>
</tr>
<tr>
<td>CL-2/P</td>
<td>140</td>
<td>0.35</td>
<td>1.00</td>
<td>50.55</td>
<td>0.19</td>
</tr>
<tr>
<td>CL-3/P</td>
<td>370</td>
<td>0.27</td>
<td>0.55</td>
<td>52.85</td>
<td>0.08</td>
</tr>
</tbody>
</table>

The increase in photocurrents after formation of the CL, indicates that a thin compact SnO$_2$ film on FTO avoids direct physical contact of electrolyte species with FTO. As a result it restricts the recombination of photoelectrons with oxidized electrolyte species. It has been reported that the implementation of a blocking layer the efficiency of DSSCs could be increased by three to four orders of magnitude [8, 16, 20]. Additionally, the deposition of a compact layer on FTO helps to improve the adhesion of the porous layer film [17, 29].

The observed decreased series resistance for the cells with CLs can be attributed to decreased electrical contact resistance (i.e., resistance to electron transfer at interfaces) between the SnO$_2$ photoelectrode and the FTO.

In study by Peng et al. [30] on TiO$_2$ blocking layers of different thickness were used. It was observed that, In DSSC with compact layer having thickness below certain threshold value (near about ~ 120 nm), the charge recombination was only partially suppressed, and does not help too much to enhance the performance of the
device. However, the increase in thickness beyond certain threshold value causes the increase in series resistance. Thus, the thickness of the blocking layer needs to be optimized to balance the above two effects.

Thus, in summary, the enhancement in $J_{SC}$ in case of DSSC with CLs as compared to the DSSC without CLs has been attributed to reduced recombination at the FTO/SnO$_2$ interface, which causes improvement in the charge collection efficiency. This may also contributes to enhancement in $V_{OC}$.

4.5-2: DSSC based on EY- Sensitized SnO$_2$ porous photoanode films: effect of porous layer thickness

Fig. 4.12 shows the current density ($J$) versus photovoltage ($V$) characteristics for all the five cells fabricated with photoanode PA1 to PA5. The photovoltaic parameters of the cells are summarized in Table 4.2.

It is observed from Table 4.2 that, the overall photovoltaic efficiency ($\eta$) of the cells increased continuously with increasing thickness of the photoanode up to PA4. It shows the best performance with $\eta$ of 0.55%. With further increase in thickness beyond PA4, the photovoltaic efficiency of the cell decreased.

Fig. 4.12: Current density Vs voltage (J-V) characteristics for solar cells constructed using Eosin-Y sensitized PA1 to PA5 under illumination.
Influence of Geometrical Thickness of Compact/Porous SnO$_2$ Photoanode Films on the Performance of Dye Sensitized Solar Cells

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Fig. 4.13: Variation of short circuit current density ($J_{SC}$) and photo conversion efficiency ($\eta$) for DSSCs based on PA1 to PA5

Table 4.2: Photovoltaic parameters for PA1 to PA5 based DSSC.

<table>
<thead>
<tr>
<th>Photoanode</th>
<th>Thickness of Photoanode (µm)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
<th>$R_s$ (KΩ)</th>
<th>$R_{sh}$ (KΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA1</td>
<td>1</td>
<td>0.29</td>
<td>0.39</td>
<td>51.03</td>
<td>0.06</td>
<td>6.10</td>
<td>22.930</td>
</tr>
<tr>
<td>PA2</td>
<td>3</td>
<td>0.33</td>
<td>0.56</td>
<td>49.35</td>
<td>0.10</td>
<td>5.72</td>
<td>150.107</td>
</tr>
<tr>
<td>PA3</td>
<td>6</td>
<td>0.37</td>
<td>1.51</td>
<td>51.83</td>
<td>0.32</td>
<td>2.03</td>
<td>66.443</td>
</tr>
<tr>
<td>PA4</td>
<td>8</td>
<td>0.35</td>
<td>2.75</td>
<td>51.99</td>
<td>0.55</td>
<td>1.14</td>
<td>42.887</td>
</tr>
<tr>
<td>PA5</td>
<td>14</td>
<td>0.35</td>
<td>1.55</td>
<td>46.57</td>
<td>0.28</td>
<td>2.36</td>
<td>42.665</td>
</tr>
</tbody>
</table>

Though, diffused reflectance spectra in Fig. 4.7 showed continuous enhancement in the scattering magnitudes from PA1-PA5, such an increasing trend did not show up in the energy conversion efficiency of the cell. Interestingly, among the photovoltaic parameters tabulated for all the characterized cells given in the Table 4.2, $J_{SC}$ and $\eta$ showed a good correlation. The same is graphically shown in Fig. 4.13, indicating that $J_{SC}$ is the main contributing parameter for the photovoltaic performance in the tested devices. Such a correlation is also reported in photoanode thickness based studies by others [31]. This inference is justified in the light of very small variation in the obtained open circuit voltage ($V_{OC}$) values for all the fabricated cells tested under constant input power.

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$J_{SC}$ is broadly, a function of the LHE of the photoanode and the electron transfer yield ($\Phi_{ET}$) [24]. $\Phi_{ET}$ is basically the product of the electron injection and electron collection efficiencies. For light scattering films previous studies by Tachibana et al, [24] reported that, increase in optical thickness of a film enhances the LHE, but its $\Phi_{ET}$ drops linearly. The overall performance of the cell depends finally on the dominant parameter of these two.

As described earlier, the optical thickness for films prepared from same SnO$_2$ paste is directly proportional to the geometrical thickness. As all other photoanode related parameters are kept constant except its thickness, the geometrical thickness of SnO$_2$ photoelectrode seems to have influenced the performance of devices significantly and is responsible for the show up of such a trend in the overall conversion efficiencies.

As observed from absorption spectra in Fig. 4.8, the LHE continuously increased with increase of thickness from PA1 to PA5. However, $\eta$ has not shown a linear variation with LHE. In view of the above and apparent inverse relation between optical thickness and $\Phi_{ET}$, the contribution of $\Phi_{ET}$ seems to have also influenced the device performance with increase in thickness of photoelectrode. Such a relation between optical thickness and $\Phi_{ET}$ is understood to have resulted from variations in constituent factors of electron transfer yield namely, charge injection and charge collection efficiencies [24].

However, the former being a remote possibility, was neglected in previous reports [24,25,28]. The latter transpires from the unevenly generated dye oxidized states in the photoelectrode, making mass transport of the redox electrolyte as the limiting step. In other words, such a happening leads to enhanced charge recombination between the conduction band (CB) electrons in SnO$_2$ and the oxidized electrolyte, resulting in the decrease of the electron collection efficiency. Another possible reason for the reduction in electron collection yield is that, the inhomogeneously excited molecules of the sensitizer increase the number of electrons injected in to the CB of SnO$_2$ and subsequently may fill the trap states on the surface of the SnO$_2$ particles. Such a filling may accelerate the charge recombination rate between electron and the redox species in the electrolyte. The
very fact that increased thickness of the SnO$_2$ electrode increases the surface area and hence the density of the surface trap states in the system, allows us to infer that the electron transfer yield would suffer a dip in such films with high light scattering.

In the results obtained in the present study, increased geometrical thickness of the film has continuously enhanced the overall cell performance from PA1 to PA4, probably because of the dominant role of $LHE$ in these films as compared to decrease in $\Phi_{ET}$. The continuous increase in $J_{SC}$ and reduction in the series resistance, (Table 4.2) for the DSSC, based on PA1 to PA4, stands testimony to such a proposition. However, for the cell based on PA5, the film thickness is nearly double that of PA4, thus increasing the density of surface trap states in these films substantially. In such a film the enhanced light scattering effects naturally have a deleterious effect on the electronic collection yield due to surface trap state assisted recombination as discussed above. Thus, the observed increase in the series resistance of the DSSC, based on PA5 as compared to that of PA4 (Table 4.2), is clearly in agreement with the analysis carried out above and so results in the decrease of both $J_{SC}$ and $\eta$ for the PA5 based DSSC. Other solar cell parameters did not show any specific correlation.

In the present study, the DSSC based on SnO$_2$ film with 8µm thickness showed the best performance, in terms of both the $J_{SC}$ and $\eta$. This indicates that, for this thickness the photoelectrode showed the optimal $LHE$ without losing much on the part of electron transfer yields. The result of this investigation further highlights the important role of geometrical thickness of the photoelectrode in DSSC and emphasizes on the optimization of this parameter for accomplishing better performance of the solar cell for a given photoanode material. The observed $\eta$ for PA4 based DSSC may be perhaps the highest for SnO$_2$ based DSSC with Eosin-Y dye as the sensitizer so far.

**4.5-3: DSSC based on EY- Sensitized SnO$_2$ compact - porous photoanode films: effect of porous layer thickness and incorporation of optimized compact layer**

From the J–V curve and efficiency value obtained for DSSCs based on photoanode with compact layer of different thicknesses, it is concluded that, the optimized thickness of the SnO$_2$ compact layer is about 140 nm. The FTO substrates
with optimized compact layer CL-2 are further used for DSSC fabrication with photoanodes of different thicknesses from PA1 to PA4.

The *J*-*V* characteristics of all DSSCs with photoanodes PA1 to PA4 and PA1 to PA4 with compact layer are shown in Fig. 4.14. Table 4.3 summarizes the detailed performance of the DSSCs fabricated with various photoanodes. It is observed that, in each case the performance of DSSC is increased after incorporation of SnO$_2$ compact layer.

![Fig. 4.14: Current density Vs voltage (J-V) characteristics for DSSCs constructed using Eosin-Y sensitized bare and with CLs, PA1 to PA4 photoanodes](image)

**Table 4.3: Photovoltaic parameters for CL-2/PA1 to CL-2-PA4 based DSSC.**

<table>
<thead>
<tr>
<th>Photoanode</th>
<th><em>V</em>$_{oc}$ (V)</th>
<th><em>J</em>$_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA1</td>
<td>0.29</td>
<td>0.39</td>
<td>51.0</td>
<td>0.06</td>
</tr>
<tr>
<td>C-PA1</td>
<td>0.35</td>
<td>1.00</td>
<td>50.5</td>
<td>0.19</td>
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<td>PA2</td>
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<td>0.56</td>
<td>49.3</td>
<td>0.10</td>
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<tr>
<td>C-PA2</td>
<td>0.36</td>
<td>1.23</td>
<td>55.1</td>
<td>0.27</td>
</tr>
<tr>
<td>PA3</td>
<td>0.37</td>
<td>1.51</td>
<td>51.8</td>
<td>0.32</td>
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<tr>
<td>C-PA3</td>
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<td>2.49</td>
<td>53.7</td>
<td>0.49</td>
</tr>
<tr>
<td>PA4</td>
<td>0.35</td>
<td>2.75</td>
<td>52.0</td>
<td>0.55</td>
</tr>
<tr>
<td>C-PA4</td>
<td>0.42</td>
<td>2.96</td>
<td>57.3</td>
<td>0.72</td>
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</table>
The DSSC fabricated with only porous SnO₂ photoanode with optimized thickness 8 μm showed $V_{OC}$ of 0.35 V, $J_{SC}$ of 2.75 mA/cm², $FF$ of 52 %, and photoconversion efficiency ($\eta$) of 0.55%. However, it is observed that the insertion of CL-2 between FTO and the porous SnO₂ film PA4, leads to increase in the $J_{SC}$ and $\eta$ simultaneously. The photovoltaic parameters for CL-2/PA4 showed $V_{OC}$ of 0.42 V, $J_{SC}$ of 2.96 mA/cm², $FF$ of 57 %, and photoconversion efficiency ($\eta$) of 0.72 %. Fig. 4.15 shows the bar graph for $J_{SC}$ and $\eta$ of DSSC based on photoanode of different thickness with and without compact layer.

**Fig. 4.15:** Bar graphs for photoconversion efficiency and Current density of DSSCs constructed using Eosin-Y sensitized bare and with CLs, PA1 to PA4 photoanodes.
4.6: Conclusions

The DSSC with the compact layer prepared by spin-coating deposition exhibited an enhanced photovoltaic parameters compared to the DSSC without the compact layer. The enhancement in $V_{OC}$ and $J_{SC}$ is attributed to improvement in the charge collection efficiency due to reduced recombination at TCO/photoanode interface.

The geometrical thickness of photoanode film also affects photovoltaic performance of DSSC. In the present study, increasing geometrical thickness of the film has continuously enhanced the overall cell performance from PA1 to PA4, probably because of the dominant role of LHE in these films as compared to decrease in $\Phi_{ET}$ until it reduced in respect of PA5. The continuous increase in $J_{SC}$ and reduction in the series resistance stands testimony to such a proposition. The DSSC based on SnO$_2$ film with 8µm thickness showed the best performance, in terms of both the $J_{SC}$ and $\eta$ indicating that, for this thickness the photoelectrode showed the optimal LHE without losing much on the part of electron transfer yields. The study highlights the important role of geometrical thickness of the compact and porous layers of photoelectrode in DSSC and puts an emphasis on optimizing this parameter. The observed $\eta$ for PA4 and CL-2/PA4 based DSSC may be perhaps the highest for SnO$_2$ based DSSC with Eosin-Y dye as the sensitizer so far.
Chapter - 4

Influence of Geometrical Thickness of Compact/Porous SnO\textsubscript{2} Photoanode Films on the Performance of Dye Sensitized Solar Cells

References:


