4.1. Introduction

In this chapter, the fabrication and characterization of working electrode are presented. The working electrode consists of a layer of porous TiO$_2$ material on FTO coated glass substrates. Various TiO$_2$ layer deposition methods, such as spray-pyrolysis, hydrothermal method and doctor-blade method have been used. The scanning electron microscopy is done for morphological characterization of these layers. X-ray diffraction technique is used to explore the phases of TiO$_2$ in the layer. Further, these electrodes have been used for DSSC fabrication and the current-voltage characterization is done to explore their actual device performance. This chapter also describes the effect of underlying layers and barrier layers on cell performance. The fabrication of dye-sensitized solar cells with Ruthenium-based sensitizer dye as absorbers are described and the effects of electrode morphology on solar cell performance are presented.

4.2. Titanium dioxide (TiO$_2$)

Titanium dioxide has been extensively used for solar energy conversion, photo-catalysis and gas sensing because of its high photo-catalytic activity, stability and suitable band-gap [349-358]. Titanium dioxide is a wide band-gap semiconductor material with a band-gap > 3 eV. Low dimensional nanostructures of titanium dioxide have been investigated for dye-sensitized solar cells due to its unique structural, electrical, and optical properties [350-366]. The one-dimensional (1D) TiO$_2$ nanostructure has attracted much attention in preparing photoelectrochemical solar cells because of its efficient charge separation and transport properties [367-373]. Dye-sensitized solar PV modules based on TiO$_2$ have achieved efficiencies $\approx 10\%$ [374]. There is much interest among the researchers worldwide in the synthesis of TiO$_2$ nanostructures (nanorods, nanowires, nanofibres, nanoflowers, nanobelts etc.) in order to improve charge collection efficiency and power conversion efficiency of DSSC.
The photo-catalytic activity of these oxide materials depend on crystal structure, morphology, particle size, surface area, and porosity. Titanium dioxide has mainly three types of crystal phases: anatase, rutile, and brookite [375, 376]. Among these phases, the anatase phase, which is a meta-stable phase, is chemically and optically active and is also suitable for photo-catalysis applications. In dye-sensitized solar cells, photo-electrodes prepared using anatase phase TiO$_2$ give better solar cell efficiency compared to those having other crystal structures [377]. Titanium dioxide particles have strong tendency to agglomerate to larger particles, which leads to a decrease in surface area. Hence, it is very important to synthesize the TiO$_2$ nanoparticles with desired crystal structures and controlled particle size. Several methods have been used for synthesis of one-dimensional TiO$_2$ nanostructures for photo-electrochemical and dye-sensitized solar cell applications [349-373]. It would be an added advantage if the required TiO$_2$ nanoparticles are synthesized at low temperatures.

Nanocrystalline TiO$_2$ has been prepared using techniques like sol-gel, hydrothermal method and reverse-micelle methods [378-381]. The nano-particles prepared using sol-gel methods are amorphous in nature and need further heat treatment to get a crystalline product. This may lead to grain growth and may also induce phase transformation. For the synthesis of anatase TiO$_2$ nanocrystallites, much attention has been paid to hydrothermal methods using amorphous TiO$_2$ [378], TiCl$_4$ [379-381], or TiOCl$_2$ aqueous solution [382], and sol-gel methods using titanium alkoxides [383, 384]. Titanium dioxide can also be obtained by hydrolysis of titanium compounds, such as titanium tetrachloride (TiCl$_4$) [385, 386] or titanium alkoxides (Ti(OR)$_4$) [272, 387].

One of the methods used here for depositing thin-layers of TiO$_2$ on FTO coated glass substrates is spray pyrolysis. The spray pyrolysis is a simple and versatile method of making thin films and multilayered films [388]. This technique had been used in research to prepare thin and thick films, ceramic coatings, and powders [388]. It had been used for several decades in the glass [389] and in solar cell production industry [390, 391]. Spray pyrolysis represents a very simple and relatively cost-effective processing method, especially with regard to equipment costs [392].

The hydrothermal method for thin-layer deposition, which is described as a technique in which reaction occurs in a pressure vessel that allows solvents such as water to be heated to temperatures above their normal boiling points [270]. Unlike conventional synthetic processes
(e.g. capping method), the hydrothermal synthesis involves much milder conditions and softer chemistry conducted at low temperatures ($\approx 200 ^\circ C$). One of the main advantages of this technique is materials with single crystalline form can be synthesized at lower temperatures. TiO$_2$ films are prepared using the Teflon lined steel autoclave. An aqueous solution of titanium isopropoxide ($\text{Ti} \{\text{OCH(CH}_3)_2\}_4$) in acidic environment is used for growth of nano structured TiO$_2$ films.

The titanium dioxide layer is one of the main components of DSSC, which is conventionally prepared by using a doctor-blade method [24, 68, 92, 393-397]. In doctor-blade method, organic additives are commonly used for colloidal TiO$_2$ paste preparation to increase porosity of the resulting TiO$_2$ thin film [397]. The doctor-blade method results in high porosity of TiO$_2$ thin film, which inherently decreases charge transfer between the TiO$_2$ thin film and electrode [68]. In this work, the mesoporous TiO$_2$ thin film was prepared, using a dense colloidal paste of TiO$_2$ nanoparticles and diluted acetic acid by a doctor-blade coating followed by drying at 80 °C and sintering at 450 °C.

4.3. Experimental details

Fluorine doped tin oxide (F:SnO$_2$/FTO) coated glass substrates having sheet resistance $\approx 10$ $\Omega/\square$ (Pilkington glass, India) were cleaned sequentially by ultrasonic treatment in detergent, deionized (DI) water, acetone and isopropyl alcohol and dried with nitrogen before TiO$_2$ film preparation.

4.3.1. Deposition by using the spray pyrolysis system

Titanium dioxide nanoparticles (Anatase titanium (IV) oxide nanopowder, < 25 nm) and other required chemicals were procured from the Sigma Aldrich Company. The precursor sol was prepared by stirring 100 mg TiO$_2$ nanoparticles in 30 ml 1-butanol and small amount of ethylene glycol (< 5 ml) is also added to improve adhesion. Before starting the spray process, the cleaned FTO substrate is heated at 500°C on a hot-plate kept below the sprayer nozzle. The sol was sprayed on the FTO substrate to deposit a layer of TiO$_2$ using spray pyrolysis system (Fig. 4.1). The deposition parameters are listed in Table 4.1. Multiple layers were deposited on the FTO substrates by spraying 5-10 ml spray sol with a break of 5-10 minutes. This step is necessary to
remove organic matter from the deposited TiO$_2$ films. TiO$_2$ film thickness is controlled by varying the spray time.

**Table 4.1: Spray deposition parameters**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray solution</td>
<td>TiO$_2$ Nanoparticles (100 mg) + 1-butanol (30 ml) + Ethylene glycol (&lt; 5 ml)</td>
</tr>
<tr>
<td>Spray temperature</td>
<td>500 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>20 psi</td>
</tr>
<tr>
<td>Spray rate (solution flow rate)</td>
<td>5 ml/min</td>
</tr>
<tr>
<td>Distance between nozzle and substrate</td>
<td>20-25 cm</td>
</tr>
</tbody>
</table>

**Figure 4.1:** Spray pyrolysis schematic diagram

**4.3.2. Deposition using the hydrothermal technique**

Very thin layers of TiO$_2$ material (50-70 nm) were deposited to be used as a seed layers in hydrothermal process. The precursor was prepared by adding 1 mL of titanium isopropoxide to a well-mixed solution containing 15 mL of HCl and 15 mL of H$_2$O, and then the whole mixture
was vigorously stirred for another 10 min until the solution became clear. Afterward, the precursor was poured into a Teflon-lined stainless steel autoclave with the FTO substrates placed at an angle against the wall with the conductive side facing down (Fig. 4.2). Hydrothermal growth was conducted at 200 °C for 3 h in an electric oven. Afterward, the FTO substrates were rinsed with deionized water and dried in ambient air.

![Schematic diagram of autoclave for deposition of TiO₂ nanorods](image)

**Figure 4.2:** Schematic diagram of autoclave for deposition of TiO₂ nanorods

### 4.3.3. Deposition by doctor-blade method

Anatase titanium (IV) oxide nanopowder having a particle size < 25 nm, 99.7% trace metals basis (Sigma-Aldrich) was used for preparing the working electrode of DSSC. The nanocrystalline TiO₂ paste was prepared by grinding TiO₂ nanopowder (12 gm) in a mortar-pestle while adding solvent (about 20 ml acetic acid (pH adjusted to 3.5 in DI water)) dropwise. The paste preparation was done in ambient air at room temperature. The paste obtained was mixed with excess ethanol (150 ml) and magnetically stirred at 350 rpm for 2-4 hours. The ultrasonication was performed for 15 minutes to homogenize TiO₂ nanoparticles. The contents in the dispersion were concentrated by evaporator at 40 °C. The DSSC working electrodes were prepared by immersing the FTO glass plates in a 40 mM aqueous TiCl₄ solution at 70 °C for 15 minutes and rinsed with DI water and ethanol. The rinsed working electrode was sintered at 450
°C for 30 minutes. A layer of nanocrystalline titania paste was deposited on the above FTO glass by doctor-blade method. The developed DSSC working electrodes were placed in ethanol for a few minutes to reduce surface irregularities, and then dried for 5 minutes at 130 °C. The samples were sintered at 450 °C for 30 minutes in ambient air. Further, the developed nanocrystalline TiO₂ electrodes were immersed in 40 mM TiCl₄ solution for 15 minutes and sintered at 450 °C for 15 minutes.

4.3.4. Assembling of DSSC

The TiO₂ working electrode was sensitized in 0.5 mM N-719 dye (Dyesol, Australia) solution (mixture of acetonitrile and methanol, volume ratio: 1:1) at 70°C for 18-20 hours in a dark room. Transparent platinum-coated counter electrodes with fill holes were procured from Dyesol (MBPT-38, Dyesol, Australia). The dye-covered TiO₂ electrode and Pt-coated counter electrode were assembled into a sandwich type cell and sealed with Surlyn (25 µm). A drop of high-stability electrolyte (EL-HSE, Dyesol, Australia) was put in the hole in the back of the counter electrode. Finally the hole was sealed by using a hot-melt aluminum baked Bynel-thermoplastic sealant (Dyesol).

4.4. Characterization

4.4.1. Morphological characterization of TiO₂ layer

4.4.1.1. Hydrothermally grown TiO₂

A thin layer of TiO₂ was obtained by spray pyrolysis, which is used as a seed layer for further deposition of TiO₂ using hydrothermal technique. The sprayed samples were characterized by scanning electron microscopy (SEM) for topographic information. From SEM image (Figure 4.3 (a) and (b)), the sprayed layer of TiO₂ looks compact having a rough surface.

This confirms that by using a spray pyrolysis technique it is possible to deposit a compact thin-film of TiO₂ with a thickness of a few tens of nanometers based on the deposition time.
The samples with a spray seed layer were used as substrates in a hydrothermal autoclave. A flower-like TiO$_2$ layer has grown on the surface after hydrothermal process as shown in the SEM image of this type of sample (Fig. 4.4). Under the acidic environment and high pressure
conditions of hydrothermal process (200 °C, 3 hrs), the morphology of seed layer completely changed as shown in the Fig. 4.4 (b). From the Figure 4.4 it is observed that there is layered structure and then the formation of TiO$_2$ flower-like structure has happened from the one-dimensional nano-rods. Due to changed morphology, which shows the layers are not interconnected, this type of samples could not be used for DSSC applications. As we know the device need interconnected particles (or grains) for better electron transport; this requirement is not fulfilled by these samples.

TiO$_2$ layer was deposited by hydrothermal method on the FTO glass without any seed layer for further experiments. The thickness the deposited TiO$_2$ layer is found to be around 2.5 µm for a deposition time of 3 hours and 45 minutes at 200 °C. The thickness of this sample was measured by a Veeco surface profilometer as shown in Fig. 4.5. The morphological study of these samples has shown that the nanorods of \( \approx 100 \) nm diameter are developed under above mentioned conditions. Titanium dioxide layers with thickness > 2.5 µm were peeled off the FTO glass substrates and could not be used for device applications.
Figure 4.4: (a) The SEM image of hydrothermally grown TiO$_2$ flower-like structures on the FTO glass; (b) Morphology change observed for the seed layer deposited by spray pyrolysis (this morphology is observed between the flower-like structures)

Figure 4.5: The surface profile of the hydrothermally processed TiO$_2$ thin film on the FTO glass substrate
Fig. 4.6 (a)-(b) shows the SEM image of hydrothermally grown nanorods on the FTO substrates. The SEM characterization shows that the TiO$_2$ nanorods are vertically aligned on the FTO glass substrates, Fig. 4.6 (a). The cross-sectional view of TiO$_2$ film is illustrated in Fig. 4.6 (b). These SEM images confirm that TiO$_2$ nanorods are densely packed. The layer deposited by hydrothermal method has rutile phase of TiO$_2$ as confirmed by XRD analysis and shown in the next section.

**Figure 4.6:** The SEM images of hydrothermally grown TiO$_2$ nanorod structures on the FTO glass without seed layer, (a) TiO$_2$ nanorods vertically aligned, (b) cross-sectional view.
4.4.1.2. Sprayed TiO$_2$ layer

Figure 4.7(a)-(c) shows the SEM of TiO$_2$ (anatase film, Thickness ~2.5 µm) deposited on FTO glass by spray pyrolysis method. The images at different locations and magnifications (Fig. 4.7) reveal that the whole FTO substrate is uniformly covered with nano-crystalline TiO$_2$ film. The film contains aggregate to a certain extent. This aggregation may be attributed to the inhomogeneous dispersion of TiO$_2$ nanoparticles during spray. The film on the surface is smooth and no micro cracks have been observed. The size of agglomerate has grown up to a few microns during the deposition process. The higher thickness ~3 µm of TiO$_2$ layer get peeled off during deposition.
4.3.1.3. Doctor-blade TiO\textsubscript{2} layer

Figure 4.8(a)-(b) shows the scanning electron micrograph of TiO\textsubscript{2} (anatase film, thickness 12\(\mu\)m) deposited on FTO glass by doctor-blade method. The images at different locations and magnifications (Fig. 4.8(a)-(b)) reveal that the whole FTO substrate is uniformly covered with nano-crystalline TiO\textsubscript{2} film. The film contains aggregate to a certain extent as shown in Fig. 4.8. This aggregation may be attributed to inhomogeneous dispersion of TiO\textsubscript{2} nanoparticles at the stage of paste formation. The aggregation is limited to quite small extent as no cracks have been observed in the film. The insert in Fig. 4.8 (b) shows a surface profile of the nanocrystalline TiO\textsubscript{2} layer obtained by the profilometer. The flatness of the profilometer data reflects the homogeneity of the TiO\textsubscript{2} nanoparticles. The TiO\textsubscript{2} film thickness is typically ~12 \(\mu\)m (insert in Fig. 4.8 (b)), average roughness is 1.67 \(\mu\)m and average surface height is 12.26 \(\mu\)m.
Figure 4.8: (a)-(b) The scanning electron micrograph of TiO$_2$ layer on FTO glass deposited by doctor-blade method (Insert in (b): Thickness measurement by surface profilometer)

4.4.2. Structural characterization of TiO$_2$ layer

4.4.2.1. Hydrothermally grown TiO$_2$

The XRD characterization of TiO$_2$ nanorod sample (200 °C, 3 hours) is done and shown in Fig. 4.9. From JCPDS 21-1276 (rutile TiO$_2$), the XRD patterns of nanocrystalline TiO$_2$ layer
shows three peaks of rutile TiO$_2$ at $2\theta = 36.116^\circ$, $2\theta = 41.261^\circ$ and $2\theta = 54.370^\circ$, which corresponds to diffraction from (1 0 1), (1 1 1) and (2 1 1) respectively. The XRD pattern shows that this TiO$_2$ has the structure in short range mesophase order which is a typical characteristic of TiO$_2$ [398].

![XRD spectra of TiO$_2$ nanorod layer](image)

**Figure 4.9:** XRD spectra of TiO$_2$ nanorod layer, three peaks of rutile TiO$_2$ at $2\theta = 36.116^\circ$, $2\theta = 41.261^\circ$ and $2\theta = 54.370^\circ$ corresponds to diffraction from (1 0 1), (1 1 1) and (2 1 1) respectively

### 4.4.2.2. Doctor-blade TiO$_2$

Figure 4.10 shows the XRD pattern of anatase TiO$_2$ film. From JCPDS 21-1272 (anatase TiO$_2$), the XRD patterns of nanocrystalline TiO$_2$ layer shows five peaks of anatase TiO$_2$ at $2\theta = 25.302^\circ$, $2\theta = 48.091^\circ$, $2\theta = 53.938^\circ$, $2\theta = 55.110^\circ$ and $2\theta = 62.746^\circ$, which corresponds to diffraction from (1 0 1), (2 0 0), (1 0 5), (2 1 1) and (2 0 4) respectively. In addition, from JCPDS 46-1088
(Tetragonal SnO$_2$), the XRD patterns of the FTO glass shows six peaks of tetragonal SnO$_2$ at $2\theta = 26.601^\circ$, $2\theta = 33.801^\circ$, $2\theta = 37.801^\circ$, $2\theta = 51.802^\circ$, $2\theta = 61.802^\circ$ and $2\theta = 66^\circ$, which corresponds to diffraction from (1 1 0), (1 0 1), (2 0 0), (2 1 1), (3 1 0) and (3 0 1) respectively.

Figure 4.10: XRD pattern of anatase TiO$_2$ layer deposited on FTO glass

4.4.3. Electrical characterization of TiO$_2$ based DSSC

The TiO$_2$ electrodes discussed above are used to assemble DSSCs according to the process mentioned in section 4.3 and tested for their photovoltaic performance.
4.4.3.1. Hydrothermal TiO$_2$ sample

Hydrothermally deposited samples are used to assemble complete DSSC using N719 dye as a sensitizer. The TiO$_2$ electrode were sensitized in the solution of acetonitrile and ethanol (v:v/1:1) for 24 hours at 70 °C. The cells were characterized using electrochemical impedance spectroscopy (EIS) under dark conditions (Fig. 4.11). The impedance spectrum is measured over a frequency range of 0.01–$10^6$ Hz with AC amplitude of 10 mV and applied bias of 0 V. The experimental impedance spectra of DSSC gives information about the charge transfer resistance in the electrolyte (low frequency range), at the TiO$_2$/electrolyte interface (middle frequency range), and at the electrolyte/Pt interface at the counter electrode (high frequency range), respectively [228]. Impedance spectra are generally modeled using an equivalent electric circuit based on a transmission line model [399].

Current-voltage measurements are done using solar simulator under AM1.5 solar spectrum. The active device area was taken as $\approx 0.1 \text{ cm}^2$ (3 mm×3 mm). Platinum coated FTO is taken as counter electrode for these measurements.

Figure 4.11: Electrochemical impedance spectra of DSSC made using TiO$_2$ nanorods
The current-voltage characteristics of DSSC based on titanium dioxide nanorods, normalized for an area of 1 cm$^2$, is shown in Fig. 4.12 (with varying thickness). Looking at the current-voltage curve it can be stated that the DSSC is quite unstable device with current decreasing slowly at lower values of voltage. With further increase in voltage values, the current starts decreasing exponentially. A list of output parameters with variation in thickness of the active layer is given in Table 4.2. The thickness of the sample is varied by different deposition time.

Figure 4.12: The current-voltage characteristics of TiO$_2$ nanorod based DSSC with varying thickness of TiO$_2$ layer (area normalized to 1 cm$^2$)

The low output parameters of hydrothermally grown TiO$_2$ nanorod based DSSCs may be due to following reasons:

1. dense nanorods offering less area for dye adsorption: confirmed by SEM analysis and visual inspection after dye adsorption
2. lower thickness than the optimum ($\approx$ 12 µm) as per available literature
3. large series resistance: there may be a dense thicker layer between nanorods and conducting surface of FTO

Further, another method for TiO$_2$ deposition, namely spray-pyrolysis has been tried out.

**Table 4.2:** The output parameters of TiO$_2$ nanorod (NR) layer based DSSC and their dependence on thickness (given in µm)

<table>
<thead>
<tr>
<th>Sample description</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSSC-H1 (TiO$_2$ NR (1.0 µm)/N719 dye)</td>
<td>0.29</td>
<td>0.265</td>
<td>37.5</td>
<td>0.03</td>
</tr>
<tr>
<td>DSSC-H2 (TiO$_2$ NR (1.5 µm)/N719 dye)</td>
<td>0.48</td>
<td>0.302</td>
<td>34.3</td>
<td>0.05</td>
</tr>
<tr>
<td>DSSC-H3 (TiO$_2$ NR (2.0 µm)/N719 dye)</td>
<td>0.53</td>
<td>0.298</td>
<td>34.7</td>
<td>0.055</td>
</tr>
<tr>
<td>DSSC-H4 (TiO$_2$ NR (2.5 µm)/N719 dye)</td>
<td>0.61</td>
<td>0.296</td>
<td>32.3</td>
<td>0.06</td>
</tr>
</tbody>
</table>

**4.4.3.2. Sprayed TiO$_2$ sample**

The dye-sensitized solar cell was made by using nanocrystalline titania particle based working electrode in the same manner as described in the experimental section (section 4.3). The current-voltage characteristic measurements have shown that these DSSCs are highly unstable (Fig. 4.13); their electrical performance degraded rapidly with time. A list of output parameters with variation in thickness of the active layer is given in Table 4.3.

**Table 4.3:** The output parameters of sprayed TiO$_2$ nanoparticles (NP) layer based DSSC and their dependence on thickness (given in µm)

<table>
<thead>
<tr>
<th>Sample description</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSSC-S1 (TiO$_2$ NP (1.0 µm)/N719 dye)</td>
<td>0.27</td>
<td>0.251</td>
<td>30.87</td>
<td>0.02</td>
</tr>
<tr>
<td>DSSC-S2 (TiO$_2$ NP (1.5 µm)/N719 dye)</td>
<td>0.33</td>
<td>0.280</td>
<td>41.29</td>
<td>0.04</td>
</tr>
<tr>
<td>DSSC-S3 (TiO$_2$ NP (2.0 µm)/N719 dye)</td>
<td>0.66</td>
<td>0.306</td>
<td>31.51</td>
<td>0.06</td>
</tr>
<tr>
<td>DSSC-S4 (TiO$_2$ NP (2.5 µm)/N719 dye)</td>
<td>0.84</td>
<td>0.305</td>
<td>30.84</td>
<td>0.08</td>
</tr>
<tr>
<td>DSSC-S5 (TiO$_2$ NP (2.8 µm)/N719 dye)</td>
<td>0.78</td>
<td>0.297</td>
<td>33.83</td>
<td>0.08</td>
</tr>
</tbody>
</table>
The low output parameters of sprayed TiO$_2$ nanoparticle based DSSCs may be due to following reasons:

1. dense nanoparticles growing as big agglomerate offering less area for dye adsorption: confirmed by SEM analysis
2. lower thickness than the optimum ($\approx$ 12 $\mu$m) as per available literature
3. low shunt resistance: short-circuit path may be available through nanospace among the bigger agglomerates
4. higher recombination as seen in a sharp decrease of current at lower voltage [400]
5. the large series resistance offered by FTO

In order to address these issues, TiCl$_4$ treatment is done after spray deposition of TiO$_2$ nanoparticle-based layer (thickness 2.8$\mu$m) on FTO substrates. The DSSC working electrodes were prepared by immersing sprayed TiO$_2$ layer into a 40 mM aqueous TiCl$_4$ solution at 70 $^\circ$C for 10 minutes and rinsed with water and ethanol. The rinsed working electrode was sintered at
450 °C for 15 minutes. The current-voltage characteristic of this sample is shown in Fig. 4.14 and corresponding output parameters are listed in Table 4.4.

![Current-Voltage Characteristics](image)

**Figure 4.14:** The current-voltage characteristics of DSSC developed using sprayed TiO$_2$ layer

<table>
<thead>
<tr>
<th>Sample description</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSSC-S6 (TiO$_2$ NP (3 µm)/N719 dye)</td>
<td>4.89</td>
<td>0.673</td>
<td>28.1</td>
<td>0.92</td>
</tr>
</tbody>
</table>

**Table 4.4:** The output parameters of DSSC fabricated using TiCl$_4$-treated sprayed TiO$_2$ layer

This improvement in performance due to TiCl$_4$ treatment is attributed to better dye absorption and relaxing of TiO$_2$ defects. In literature, improvements in photon-to-current conversion efficiencies of DSSCs using TiCl$_4$-treated TiO$_2$ films were attributed to enhanced film thickness and light scattering [401]. Further, the luminescence measurements reported in the literature provide experimental evidence that TiCl$_4$ treatment suppresses surface defect states that are likely to be associated with oxygen vacancies [402].

There is significant improvement in photovoltaic performance of spray deposited thin films as compared to hydrothermally prepared, further improve is restricted in spray deposited films
due to pealing of films at higher thickness (> 3µm). So to get higher thickness films, well known doctor blade method is adopted for further study.

4.4.3.3. Doctor-blade TiO$_2$ layer

Electrical characterization for DSSC based on doctor-blade TiO$_2$ layer is presented in Fig. 4.15. A list of output parameters with variation in thickness of TiO$_2$ layer is given in Table 4.5.

Table 4.5: The output parameters of doctor-blade made TiO$_2$ layer based DSSC and their dependence on thickness (given in µm)

<table>
<thead>
<tr>
<th>Sample description</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSSC-D1 (TiO$_2$ NP (10 µm)/N719 dye)</td>
<td>13.02</td>
<td>0.613</td>
<td>19.54</td>
<td>1.56</td>
</tr>
<tr>
<td>DSSC-D2 (TiO$_2$ NP (11 µm)/N719 dye)</td>
<td>13.85</td>
<td>0.616</td>
<td>17.61</td>
<td>1.50</td>
</tr>
</tbody>
</table>

Figure 4.15: The current-voltage characteristics of DSSC developed using doctor-blade TiO$_2$ layer
The low fill factor and efficiencies of doctor-blade made TiO$_2$ nanoparticle layer based DSSCs may be due to following reasons:

1. low shunt resistance: short-circuit path may be available through nanospace among the agglomerates
2. large series resistance

### 4.4.3.4. Doctor-blade TiO$_2$ layer with sputtered blocking layer

As described in the introduction, the low efficiencies of the cells are due to the recombination losses and back-electron transfer to the electrolyte from the FTO substrate. In order to achieve better efficiencies, the losses should be prevented [403, 404]. Transfer of electrons to the electrolyte is inhibited by depositing compact TiO$_2$ blocking layer below the porous nanocrystalline TiO$_2$ [404-406]. The electron losses are shown in the schematic diagram in Fig. 4.16 and the Fermi level shift is shown in Fig. 4.17. Schematic illustration of the direct route for electron transfer to electrolyte via the nanocrystalline TiO$_2$ and the indirect route via the conducting glass substrate is shown in Fig. 4.16. The second route is expected to become important under open circuit conditions as explained through the Fig. 4.17.

![Figure 4.16: Schematic illustration of the direct route for electron transfer to $I_n^-$ via the nanocrystalline TiO$_2$ with the indirect route via the FTO glass substrate [404]](image)

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Figure 4.17: Schematic description of the illuminated DSSC in the absence of a blocking layer. The TiO$_2$ label refers to the layer of dye-sensitized nanocrystalline TiO$_2$ (a) Short circuit condition, (b) Open circuit condition [404]

Under short circuit conditions the Fermi level in the FTO is pinned close to the Fermi level of redox electrolyte as a consequence of the rapid electron-transfer kinetics at the platinum counter electrode (Fig. 4.17 (a)). The electron quasi Fermi level ($\nu$E$_F$) in most of the nanocrystalline film is much higher than at the FTO contact, so that electron transfer to electrolyte takes place predominantly in the bulk of the porous film. Under open circuit conditions, the Fermi level in the FTO moves up as the electron quasi Fermi level in the nanocrystalline film rises due to the establishment of a photostationary state in which the rate of electron injection by the sensitizer dye is balanced by the back transfer of electrons to electrolyte (Fig. 4.17 (b)) [404].

In order to improve efficiencies, a blocking layer of TiO$_2$ (thickness $\approx$70 nm) has been deposited by sputtering technique before depositing TiO$_2$ using doctor-blade method. This thickness is chosen on the basis of literature available [407]. A thin layer of Titanium metal was sputtered on FTO substrates by DC magnetron (HHV make vacuum system, Excel Instruments make sputter gun) of 2” size with applied power of 150 W. These samples with Ti metal were oxidized by heat treatment at 450°C for $\approx$ 2.5 hours. Electrical characterization for DSSC based
on doctor-blade TiO$_2$ layer along with the blocking layer is presented in Fig. 4.18. A list of output parameters with variation in thickness of TiO$_2$ layer is given in Table 4.6.

**Table 4.6:** The output parameters DSSC fabricated from doctor-blade made TiO$_2$ layer on blocking layer and their dependence on thickness (given in µm)

<table>
<thead>
<tr>
<th>Sample description</th>
<th>J$_{sc}$ (mA/cm$^2$)</th>
<th>V$_{oc}$ (V)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSSC-D-B1 (TiO$_2$ NP (7 µm)/N719 dye)</td>
<td>1.68</td>
<td>0.660</td>
<td>45.24</td>
<td>0.50</td>
</tr>
<tr>
<td>DSSC-D-B2 (TiO$_2$ NP (10 µm)/N719 dye)</td>
<td>3.64</td>
<td>0.678</td>
<td>36.21</td>
<td>0.89</td>
</tr>
<tr>
<td>DSSC-D-B3 (TiO$_2$ NP (12 µm)/N719 dye)</td>
<td>5.29</td>
<td>0.702</td>
<td>35.9</td>
<td>1.33</td>
</tr>
</tbody>
</table>

**Figure 4.18:** The current-voltage characteristics of DSSC developed using doctor-blade TiO$_2$ layer

As expected the blocking layer has reduced short-circuit current density, but at the same time, the fill factor has improved. So it can be concluded from these experiments that blocking
layer reduces nanospace in between the agglomerate and conducting FTO substrates. The results are in accordance with the literature [406].

Further improvement was expected from titanium tetrachloride (TiCl$_4$) treatment of the porous TiO$_2$ layer prepared by doctor-blade technique on the sputtered blocking layer ($\approx$ 50 nm). The DSSC working electrodes were prepared by immersing doctor-blade made TiO$_2$ layer into a 40 mM aqueous TiCl$_4$ solution at 70 °C for 10 minutes and rinsed with water and ethanol. The rinsed working electrode was sintered at 450 °C for 10-15 minutes. Electrical characterization for DSSCs these electrodes are presented in Fig. 4.19. The current-voltage characteristic measurements show that these DSSCs are better in terms of stability. A list of output parameters with variation in thickness of TiO$_2$ layer is given in Table 4.7.

![Figure 4.19: The current-voltage characteristics of DSSC developed using doctor-blade TiO$_2$ layer (with blocking layer ($\approx$ 50 nm) and TiCl$_4$ treatment)](image)

A list of output parameters with variation in thickness of TiO$_2$ layer is given in Table 4.7.
Table 4.7: The output parameters DSSC fabricated from TiCl$_4$ treated doctor-blade made TiO$_2$ layer on blocking layer ($\approx 50$ nm) and their dependence on thickness (given in µm)

<table>
<thead>
<tr>
<th>Sample description</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSSC-D-B-T1 (TiO$_2$ NP (10 µm)/N719 dye)</td>
<td>5.3</td>
<td>0.649</td>
<td>47.67</td>
<td>1.64</td>
</tr>
<tr>
<td>DSSC-D-B-T2 (TiO$_2$ NP (12 µm)/N719 dye)</td>
<td>7.2</td>
<td>0.672</td>
<td>59.9</td>
<td>2.9</td>
</tr>
</tbody>
</table>

4.4.4. Optical characterization of TiO$_2$ layer

The absorption and transmission measurements were done for the nanocrystalline TiO$_2$ coated FTO glass with dye and without dye using a UV-Vis spectrophotometer (UV-2600, Shimadzu). The solid line represents absorption without dye sensitization (Fig. 4.20), whereas the dashed line represents the absorption spectrum after loading dye molecules on the TiO$_2$ working electrode.

![Figure 4.20: UV-Vis absorption spectra of nanocrystalline TiO$_2$ working electrode without dye sensitization and N719 dye loaded TiO$_2$ electrode (Insert: transmission spectra for the same)](image-url)
Figure 4.20 illustrates that light absorption increases in the 400-700 nm wavelength range for a dye-sensitized TiO\textsubscript{2} electrode compared to that for a bare TiO\textsubscript{2} working electrode. The absorption peak is observed at ~520 nm, which is a characteristic of N719 dye. The insert shows transmission spectra of bare nanocrystalline TiO\textsubscript{2} working electrode and N719 dye-loaded TiO\textsubscript{2} electrode (Fig. 4.20). The TiO\textsubscript{2} nanoparticle layer was hazy and whitish in nature. The incident light below 380 nm is absorbed by the band-to-band absorption. The transmission curve shifts downward when the TiO\textsubscript{2} electrode is dye-sensitized, due to absorbing nature of dye molecules in the visible range.

4.4.5. Capacitance-voltage characterization of DSSC

Capacitance–voltage (C-V) measurement is an important tool for understanding the material aspects of a semiconductor device. Generally capacitance is measured in the reverse bias (Mott-Schottky) condition to determine the potential difference between the Fermi level of TiO\textsubscript{2} and redox potential of electrolyte ($V_{bi}$). Further, C-V measurement also indicates that the effective carrier concentration ($N$) in the conduction band of working electrode of DSSC. Figure 4.21 shows the C-V of developed DSSC.

![Graph](image)

**Figure 4.21**: Mott-Schottky plot of DSSC (Insert: C-V characteristics of DSSC)
The slope and its intersection on the abscissa in the Mott-Schottky plot shown in Fig. 4.21 for the DSSC, gives the carrier concentration \((N)\) under dark conditions and the potential difference \((V_{bi})\) respectively. A linear fit was performed on the experimental data obtained to explore the charge carrier density and barrier potential. The \(N\) value is calculated as \(\approx 10^{11} \text{ cm}^{-3}\) and the value of \(V_{bi} - 2 kT/q\) is equal to 0.6 eV, which corresponds to \(V_{bi} = 0.55\) eV. The magnitude of charge carrier density is in agreement with the insulating nature of \(TiO_2\) material under dark conditions.

The experimental non-linear plot of \(C^{-2}\) versus \(V\) (Fig. 4.20) results from the surface state effects, recombination effects and non-negligible contributions of the Helmhotz layer to the interfacial capacitance. The insert in Fig. 4.21 shows an increase in the capacitance of DSSC with increasing bias voltage, which is in agreement with existing literature [280].

\[\text{4.5. Theoretical Performance Prediction Model}\]

The terminal equation for current-voltage characteristics of the DSSC based on two-diode model is described in section 3.3 and is given below. A modification is made in the previous model as per the equivalent circuit shown in Fig. 4.22. In order to visualize the effect of series resistance, the series resistance term is added in series with all other resistive effects as given by Fig. 4.22 and Eq. (4.4).

\[
I = I_{ph} - I_i \left\{ \exp \left( \frac{q(V+IZ)}{nk_BT_C} \right) - 1 \right\} - I_r \left\{ \exp \left( \frac{q(V+IZ)}{nk_BT_C} \right) - 1 \right\} - (V + IZ) \left( j\omega C_i + 1/R_{sh} \right) \quad (4.1)
\]

where,

\[
I_{ph} = \left[ I_{SC} + K_i (T_C - T_{Ref}) \right] \lambda \quad (4.2)
\]

\[
I_{SC} = \frac{[1-r(\lambda)]q\Phi_D\lambda \alpha [-L_n \alpha \cosh \left( \frac{d}{L_m} \right) + \sinh \left( \frac{d}{L_m} \right) + L_n \alpha \exp(-d\alpha)]}{A(1-L_e^2\alpha^2) \cosh \left( \frac{d}{L_m} \right)} \quad (4.3)
\]

\[
Z = \frac{1}{R_{rec} + j\omega L_{RS}^{-1}} + R_S \quad (4.4)
\]

\[
Z_S = \frac{1}{j\omega C_E + 1/R_E} + \frac{1}{j\omega C_{CE} + 1/R_{CE}} + W \quad (4.5)
\]

\[
W = \sigma \omega^{-\frac{1}{2}} (1 - j) \quad (4.6)
\]
A short description of the dynamic resistance prediction model is given below. The detailed treatment is given in section 3.3. The equation (4.1) can be modified under static condition ($\omega \approx 0$) as given below:

$$I = I_{ph} - I_t \left\{ \exp \left( \frac{q(V + iZ)}{n k_B T_C} \right) - 1 \right\} - I_r \left\{ \exp \left( \frac{q(V + iZ)}{n k_B T_C} \right) - 1 \right\} - \left( \frac{V + iZ}{R_{sh}} \right)$$  \hspace{1cm} (4.7)

In order to estimate the dynamic resistance, Eq. (4.7) is subjected to following boundary conditions:

(i)  \hspace{8pt} 0 < V < V_m \text{ and } I_m < I < I_{SC}

(ii)  \hspace{8pt} V_m < V < V_{OC} \text{ and } 0 < I < I_m

At any two operating points ($V_1$, $I_1$) and ($V_m$, $I_m$) on a single I-V curve, the relationships between $V$ and $I$ are:

$$V_1 = \frac{n k_B T_C}{q} \times \ln \frac{R_{sh}[I_{ph} + I_t + I_r - I_1] - 1}{R_{sh/I_r}} \times I_1 Z$$  \hspace{1cm} (4.8)

$$V_m = \frac{n k_B T_C}{q} \times \ln \frac{R_{sh}[I_{ph} + I_t + I_r - I_m] - 1}{R_{sh/I_r}} \times I_m Z$$  \hspace{1cm} (4.9)

At any two operating points ($V_m$, $I_m$) and ($V_2$, $I_2$) on a single I-V curve, the relationship between $V$ and $I$ are:

$$V_m = \frac{n k_B T_C}{q} \times \ln \frac{R_{sh}[I_{ph} + I_t + I_r - I_m] - 1}{R_{sh/I_r}} \times I_m Z$$  \hspace{1cm} (4.10)

$$V_2 = \frac{n k_B T_C}{q} \times \ln \frac{R_{sh}[I_{ph} + I_t + I_r - I_2] - 1}{R_{sh/I_r}} \times I_2 Z$$  \hspace{1cm} (4.11)

Since a shunt resistance is normally much greater than series impedance $Z$. Thus $R_{sh}[I_{ph} + I_t + I_r - I_1] >> I_1 Z$ and $R_{sh}[I_{ph} + I_t + I_r - I_2] >> I_2 Z$. Therefore,
\[
Z = \frac{v_1 - v_2}{l_2 - l_1} - \frac{(m-n)k_{\text{BT}}c}{q} \times \ln \left[ \frac{I_{\text{ph}} + l_i + l_e - l_2}{I_{\text{ph}} + l_i + l_e - l_1} \right]
\] (4.12)

The first term of Eq. (4.12) is essentially a slope at any operating point, or the external dynamic resistance, \( R_D \). The second term is the internal dynamic resistance, \( R_d \) of the DSSC.

4.6. Validation and analysis of the model developed

4.6.1. Current-voltage characterization

The curve (marked by open circles) in Fig. 4.23 represents the experimental I-V characteristics of developed DSSC. The model summarized in section 4.4 was used to predict I-V response of developed DSSC. The parameters used in the simulation are given in Table 4.8.

![Figure 4.23: Simulated I-V curve matching well with the experimental data (Insert: dark I-V characteristics of developed DSSC)](image)

Table 4.8: Values of model parameters used for simulation of I-V curves and Nyquist plots

| \( I_{\text{ph}} \) (mA/cm\(^2\)) | \( I_i \) (A/cm\(^2\)) | \( I_r \) (A/cm\(^2\)) | \( C_i \) (F) | \( R_{\text{sh}} \) (\(\Omega\)) | \( R_{\text{rec}} \) (\(\Omega\)) | \( R_E \) (\(\Omega\)) | \( C_E \) (\(\mu\text{F}\)) | \( R_{CE} \) (\(\Omega\)) | \( C_{CE} \) (\(\mu\text{F}\)) | \( \sigma \) (\(\Omega\) s\(^{-1/2}\)) | \( R_S \) (\(\Omega\)) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 7.2 | 8.57 \times 10^{-15} | 9.26 \times 10^{-10} | 10 | 3000 | 3.9 | 60.61 | 0.51 | 225.9 | 0.8 | 80 | 12.1 |
It is evident from Fig. 4.23 that the theoretical model given in section 4.5 agrees quite well with the experimental data. The experimentally observed cell efficiency of 2.9% \( J_{SC} = 7.2 \) mA/cm\(^2\); \( V_{OC} = 672 \) mV; \( P_{MAX} = 2.9 \) mW; FF = 59.9%; \( R_S = 22 \) \( \Omega \) is in good agreement with the simulated parameters of a DSSC having efficiency of 2.9% \( J_{SC} = 7.2 \) mA/cm\(^2\); \( V_{OC} = 672.5 \) mV; \( P_{MAX} = 2.9 \) mW; FF = 59.89%; \( R_S = 22.2 \) \( \Omega \). The experimental and simulated I-V curves were fitted by means of the parameters \( R_S, R_{sh}, D_i \) and \( D_r \). The insert in Fig. 4.23 represents the dark I-V characteristics of the DSSC. The fitted ideality factor reflects a combination of recombination and diffusion currents where the \( n > 2 \) corresponds to the dominance of recombination current, which signifies non-ideal behavior in the I-V characteristics. The non-ideality causes the limitation of the photocurrent generated in the solar cell by diffusion of iodide-triiodide ion within nanocrystalline TiO\(_2\) layer.

4.6.2. Electrochemical impedance spectroscopy

In the Nyquist plots of the fabricated DSSC, the respective electrochemical steps with different time constants are represented by the semicircles as shown in Fig. 4.24. The tri-iodide diffusivity was obtained by fitting the experimental EIS spectra under illumination to an appropriate electrical analogue [338, 339]. The diffusion of \( I_2^- \) in the electrolyte is usually well described by the Nernst diffusion impedance, characterized by Warburg parameter and a characteristic diffusion time constant [282, 340]. Due to excess of \( I^- \) ions compared to \( I_2^- \), former does not contribute to the diffusion impedance [341].

The low-frequency semi-arc in the Nyquist plot represents the electrolyte-platinum interface and may be expressed as a charge-transfer resistance and a double layer capacitance [330]. Impedance spectra are simulated over a frequency range of 0.01–10\(^6\) Hz with AC amplitude of 10 mV. The values of model parameters used in the simulation are summarized in Table 4.8. The shunt resistance, \( R_{sh} \) can be estimated from the slope of the I-V curve near short-circuit current point, which is typically of the order of 10\(^3\) \( \Omega \) for a highly efficient solar cell. The values of \( I_i \) and \( I_r \) are found to be of the orders of 10\(^{-9}\) and 10\(^{-5}\) A/cm\(^2\), respectively. The inductor \( L \) is 1 \( \mu \)H. The double-layer capacitance \( C_i \) is determined to be of the order of 10 F [330]. The large capacitance at TiO\(_2\)/dye/electrolyte interface (\( C_i \)) result from the large surface area of the nanocrystalline TiO\(_2\) structure [330]. The length between the intercepts at the real axis corresponds to the charge-transfer resistance (\( R_{ct} \)) of the component. The double-layer
capacitance \( (C_i) \) is determined from the characteristic frequency, \( C_i = \frac{1}{(R_{ct} \omega_{max})^{-1}} \) [345]. The resistance elements \( R_{rec}, R_E, R_{CE}, \) and \( R_S \) are typically several ohms for a highly efficient solar cell. The interfacial capacitances \( C_E \) and \( C_{CE} \) are of the orders of 1 mF and 1 µF, respectively.

*Figure 4.24:* The EIS of simulated DSSC matches well with experimental data

### 4.6.3. Effect of illumination on steady and dynamic parameters

The model proposed in section 4.4 is used to estimate the I-V characteristics of the DSSC. The static parameters \( (I_{SC}, V_{OC}, P_{MAX} \) and \( R_S \)) of the fabricated DSSC are estimated under STC conditions. The simulated current-voltage characteristics of the fabricated DSSC are shown in Fig. 4.25 as a function of incident illumination at constant cell temperature.

The values of the dynamic resistance at MPP are computed using the values of \( I_{ph}, I_{SC} \) and \( R_S \). The dynamic resistance of DSSC cell is calculated in an effective manner using a mathematical model given in section 3.3, and reported in Table 4.9. From the data given in Table 4.9, the series resistance, \( R_S \) shows a decreasing trend (from 77.8 Ω to 22.2 Ω) continuously with increase in the intensity of illumination. The dynamic resistance is calculated from the theoretical model for various illumination levels as listed in Table 4.9. It is found that the dynamic resistance of fabricated DSSC decreases from 440.7 Ω to 78.6 Ω with an increase in illumination level from 20 mW/m\(^2\) to 100 mW/m\(^2\).
Table 4.9: Effect of illumination on steady state and dynamic parameters of DSSC calculated at 298.14 K

<table>
<thead>
<tr>
<th>Illumination (mW/cm²)</th>
<th>J_SC (mA/cm²)</th>
<th>V_OC (mV)</th>
<th>P_MAX (mW)</th>
<th>R_S (Ω)</th>
<th>R_d (Ω)</th>
<th>Efficiency, η (%)</th>
<th>I_i (A/cm²)</th>
<th>I_r (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.4</td>
<td>585.0</td>
<td>0.41</td>
<td>77.8</td>
<td>440.7</td>
<td>2.03</td>
<td>8.57×10⁻¹⁵</td>
<td>9.26×10⁻¹⁰</td>
</tr>
<tr>
<td>40</td>
<td>2.9</td>
<td>628.6</td>
<td>1.00</td>
<td>38.2</td>
<td>223.8</td>
<td>2.50</td>
<td>8.57×10⁻¹⁵</td>
<td>9.26×10⁻¹⁰</td>
</tr>
<tr>
<td>60</td>
<td>4.3</td>
<td>649.0</td>
<td>1.70</td>
<td>28.8</td>
<td>152.7</td>
<td>2.83</td>
<td>8.57×10⁻¹⁵</td>
<td>9.26×10⁻¹⁰</td>
</tr>
<tr>
<td>80</td>
<td>5.8</td>
<td>662.5</td>
<td>2.30</td>
<td>24.7</td>
<td>109.2</td>
<td>2.87</td>
<td>8.57×10⁻¹⁵</td>
<td>9.26×10⁻¹⁰</td>
</tr>
<tr>
<td>100</td>
<td>7.2</td>
<td>672.5</td>
<td>2.90</td>
<td>22.2</td>
<td>78.6</td>
<td>2.90</td>
<td>8.57×10⁻¹⁵</td>
<td>9.26×10⁻¹⁰</td>
</tr>
</tbody>
</table>

The short-circuit current density (J_SC) increases from 1.4 to 7.2 mA/cm² with an increase in illumination level from 20 mW/m² to 100 mW/m². A logarithmic dependence of V_OC (changes from 585 mV to 672.5 mV) on the illumination is observed in the DSSC and shown in Fig. 4.25. The dependence of V_OC on the illumination (λ) is given by [347]:

Figure 4.25: Effect of illumination on the I-V characteristics of DSSC
\[ V_{OC} \alpha \frac{k_B T_C}{q} \ln (\lambda) \]  

(4.13)

A detailed discussion for dependence of \( J_{SC} \) and \( V_{OC} \) on illumination is given in section 3.3. The open-circuit voltage is also dependent on the saturation current density of the recombination diode and described in section 3.3.

**4.6.4. Effect of temperature on steady-state and dynamic parameters**

Figure 4.26 shows the effect of cell temperature (\( T_C \)) on I-V characteristics of DSSC. The steady-state and dynamic parameters are estimated from the proposed model at different temperatures and are listed in Table 4.10.

**Table 4.10:** Effect of temperature on steady state and dynamic parameters of DSSC at 100 mWcm\(^{-2}\)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( I_{SC} ) (mA/cm(^2))</th>
<th>( V_{OC} ) (mV)</th>
<th>( P_{MAX} ) (mW)</th>
<th>( R_S ) ((\Omega))</th>
<th>( R_d ) ((\Omega))</th>
<th>Efficiency, ( \eta ) (%)</th>
<th>( I_i ) (A/cm(^2))</th>
<th>( I_r ) (A/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>7.2</td>
<td>672.5</td>
<td>2.9</td>
<td>17.2</td>
<td>78.6</td>
<td>2.9</td>
<td>8.57×10(^{-15})</td>
<td>9.26×10(^{-10})</td>
</tr>
<tr>
<td>303</td>
<td>7.2</td>
<td>645.0</td>
<td>2.7</td>
<td>22.7</td>
<td>79.6</td>
<td>2.7</td>
<td>2.31×10(^{-14})</td>
<td>1.52×10(^{-9})</td>
</tr>
<tr>
<td>308</td>
<td>7.3</td>
<td>617.2</td>
<td>2.5</td>
<td>23.1</td>
<td>75.3</td>
<td>2.5</td>
<td>6.06×10(^{-14})</td>
<td>2.46×10(^{-9})</td>
</tr>
<tr>
<td>313</td>
<td>7.3</td>
<td>588.8</td>
<td>2.3</td>
<td>23.5</td>
<td>71.8</td>
<td>2.3</td>
<td>1.54×10(^{-14})</td>
<td>3.92×10(^{-9})</td>
</tr>
</tbody>
</table>

The increase in the DSSC working temperature can influence the charge transfer and the recombination kinetics, resulting in change in \( V_{OC} \) and \( J_{SC} \). For a given solar irradiation, the increase in cell temperature causes an insignificant increase in \( J_{SC} \) (insert of Fig. 4.26). The small increase in \( J_{SC} \) (from 7.2 mA/cm\(^2\) to 7.3 mA/cm\(^2\)) with cell temperature is due to a reduction in the gap between Fermi-level of TiO\(_2\) and the redox potential which causes an enhanced electron transfer from the excited state of dye (LUMO) to the conduction band of TiO\(_2\) semiconductor. Figure 4.26 also shows that, \( V_{OC} \) decreases significantly with increase in cell temperature and this reduction is mainly attributed to reduction in the gap between Fermi-level of TiO\(_2\) and redox potential. A detailed description of effect of temperature on the \( J_{SC} \) of a DSSC is given in section 3.3.
Figure 4.26: The effect of cell temperature on the I-V curve of DSSC (Insert: effect of cell temperature on current density)

Figure 4.27 show that the $I_r$ plays a critical role in deciding the performance of the DSSC. The current-voltage characteristics (Fig. 4.23) of developed DSSC indicate a lower shunt resistance responsible for a significant difference in $I_{SC}$ to $I_{MAX}$ for an efficient DSSC. A higher shunt resistance and lower series resistance is needed. The experimental and theoretically observed shunt resistance of developed solar cell is 1363 Ω, which is significantly lower than the efficient DSSC [153, 330].

It should be mentioned here that the saturation current ($I_s$) for the recombination diode ($D_r$) in a two-diode model is mainly dependent on the cell temperature (as described in section 3.3). As temperature increases, $I_s$ increases, which contributes to a further decline in DSSC output performance (Fig. 4.27).
4.7. Conclusions

The development and characterization of the working electrode and complete device is presented. The working electrode consisted of a layer of porous TiO$_2$ material on FTO coated glass substrates. Various TiO$_2$ layer deposition methods, such as spray-pyrolysis, hydrothermal method and doctor-blade method have been tried out. The scanning electron microscopy is done for morphological characterization of these layers. X-ray diffraction technique is used to explore the phases of TiO$_2$ in the layer. Further, these electrodes have been used for DSSC fabrication and the current-voltage characterization is done to explore their actual device performance. This chapter also describes the effect of underlying layers and barrier layers on cell performance. The fabrication of dye-sensitized solar cells with Ruthenium-based sensitizer dye as absorbers are described and the effects of electrode morphology on solar cell performance are presented. This study also presented the steady-state current–voltage characteristics, electronic and ionic processes and dynamic response of a dye-sensitized solar cell (DSSC) fabricated using TiO$_2$ nanoparticles. A dye-sensitized solar cell with 12.26 µm thick TiO$_2$ layer was fabricated. It had a power conversion efficiency of 2.9% under AM1.5 conditions, with a photo-generated current density ($J_{SC}$) of 7.2 mAcm$^{-2}$, and an open-circuit voltage ($V_{OC}$) of 672 mV. The entire electrochemical cell behavior (at the TiO$_2$-electrolyte interface, diffusion of electrolyte and

![Figure 4.27: Influence of saturation current $I_t$ on the electrical performance of DSSC](image-url)
charge transfer at counter electrode) was mathematically modeled using an AC electrical
equivalent circuit. The effect of temperature and illumination on the steady state and dynamic
parameters of DSSCs was also studied. A positive temperature coefficient of dynamic resistance
is observed. The dynamic resistance of DSSC decreases from 440.7 Ω to 78.6 Ω with increase in
illumination level from 20 mWcm$^{-2}$ to 100 mWcm$^{-2}$. It is found that the saturation current of
the rectifying diode and the saturation current of the recombination diode are responsible for the
recombination losses and have major influence on the overall conversion efficiency.