Chapter 2
Experimental Techniques

2.1. Introduction

This chapter describes the different methods for TiO$_2$ film deposition and their characterization techniques. Film deposition methods, such as, thermal evaporation, sputtering technique, spray pyrolysis, hydrothermal technique and doctor blade method are briefly described. Various characterization techniques, such as, stylus profilometry, X-ray diffraction (XRD), Scanning electron microscopy (SEM), Atomic force microscopy (AFM), UV-Vis-NIR spectrophotometer, Impedance spectroscopy, Capacitance-voltage measurements and Current-voltage measurements for developed dye-sensitized solar cells are described. This chapter also includes deposition and characterization techniques for metallic thin-films for plasmonics applications.

Synthesis of wide bandgap semiconductor nano-structured films has attracted much attention because of their potential applications in novel photovoltaic devices including ordered hybrid bulk hetero-junction as well as dye- and quantum-dot-sensitized solar cells [210-224]. Synthesis of 1D TiO$_2$ nanostructures may be achieved by various routes including sol–gel methods, template-assisted methods, hydrothermal/solvothermal approaches, and by electrochemical methods [225-245]. The processing method that one selects to prepare thin layers depends to a large extent, on cost, but even more important is the end application.

2.2. Methodology of sample preparation and characterization

A flow chart describing the sample preparation and characterization steps is given in Fig. 2.1.
Figure 2.1: Flowchart describing the sample preparation and characterisation steps
2.3. Fabrication techniques

2.3.1. Thermal evaporation method

A thermal evaporator uses an electric resistance heater to melt the material and raise its vapor pressure to a useful range. This process is performed in high vacuum ($\approx 5 \times 10^{-6}$ Torr), to allow the vapor to reach the substrate without reacting with or scattering against other gas-phase atoms in the chamber, and reduce the incorporation of impurities from the residual gas in the vacuum chamber [246]. A schematic diagram of the thermal evaporation system is shown in Fig. 2.2.

![Schematic diagram of thermal evaporation system](image)

**Figure 2.2:** Schematic diagram of thermal evaporation system
The materials with a much higher vapor pressure than the heating element can only be deposited without contamination of the film.

The vacuum system consists of a rotary pump followed by diffusion pump. The vacuum measurement is conducted through a Pirani gauge (760 Torr – $10^{-3}$ Torr) followed by a Penning gauge ($10^{-3}$ Torr – $10^{-9}$ Torr). The circulation of the chilled water is maintained throughout the course of the experiment. Substrate heater is used for heating the substrate during deposition. Thin films of Ag have been prepared by using a thermal evaporator system, HHV BC300 provided by Hind High Vacuum Co. Ltd., India.

### 2.3.2. Sputtering technique

Sputtering is a physical vapor deposition (PVD) method for depositing thin films. This involves ejecting atoms from a "target" material onto a "substrate" as shown in Fig. 2.3. The sputtering process consists of the bombardment of target material by fast moving, heavy, inert gas ions from the plasma (Ar gas). The bombarding ions cause atoms to be ejected from the target material by momentum transfer between the colliding ions and the target atoms. During DC-diode sputtering the atoms that leave the target with typical energies of 5 eV undergo gas scattering events in passing through the plasma gas. A number of processes occur when the ions collide with the target material. Some of the bombarding ions reflect back and are neutralized and due to repeated energy-reducing collisions they eventually thermalize or reach the kinetic energy of the surrounding gas. The mobility of the incident atoms arriving at the substrate is highly dependent upon the sputtering parameters (pressure and power), the temperature of the substrate, the distance between the target and substrate, and the surface. The sputtered target atoms which are deposited at the substrate form the resulting thin film [247]. The DC sputtering system described here is used for preparation of Ti metal of thickness 50-100 nm. The deposited Ti film is further annealed in O$_2$ environment at 450-500°C to obtain a blocking layer of TiO$_2$ for DSSC.
2.3.3. Hydrothermal Process

The hydrothermal process includes various techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures. Hydrothermal method can be defined as a method of synthesis of single crystals that depends on the solubility of minerals in hot water under high pressure. Many groups have used the hydrothermal method to prepare TiO$_2$ nanoparticles [248-255]. Besides TiO$_2$ nanoparticles, TiO$_2$ nanorods have also been synthesized with the hydrothermal method [256-267]. Zhang et al. obtained TiO$_2$ nanorods by treating a dilute TiCl$_4$ solution at 333-423 K for 12 h in the presence of acid or inorganic salts [256]. The
ordered ZnO nanorods of high uniformity in diameter and height have been grown by hydrothermal technique [268]. Nanocrystalline SnO$_2$ was synthesized by a Sn/H$_2$O$_2$/H$_2$SO$_4$ hydrothermal oxidation at 150°C [269].

Figure 2.4: Hydrothermal autoclave
Advantages of the hydrothermal method over other types of thin film deposition methods include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapor pressure near their melting points can also be grown by the hydrothermal method. The method is suitable for the growth of large crystals while maintaining good control over their composition. Disadvantages of the method include the need of expensive autoclaves, and the impossibility of observing the crystal during its growth [270].

2.3.4. Spray pyrolysis

Spray pyrolysis is a process in which a thin film is deposited by spraying a solution on a heated surface (≈ 500 °C), where the constituents react to form a chemical compound. The chemical reactants are selected such that products other than the desired compound are volatile at the temperature of deposition [271]. The process is particularly useful for the deposition of oxides and used here for the deposition of nanocrystalline TiO$_2$ layer on FTO glass substrates. The spray pyrolysis equipment consists of an atomizer, precursor solution, substrate heater, and temperature controller [272]. The method involves spraying a solution containing precursors onto a heated substrate. Sprayed droplets or residual particles reaching the hot surface undergo pyrolytic decomposition and form a single or a polycrystalline film. The quality and properties of the films depend largely on the process parameters. The most important parameter is the substrate surface temperature [273-275]. The spray pyrolysis system (HOLMARC Model- HO-TH-04) used for depositing titania layer is shown in Fig. 2.5.

The general simplified scheme for spray pyrolysis deposition consists of three processing steps as listed below:

1) Atomization of the precursor solution
2) Aerosol transport of the droplet
3) Decomposition of the precursor to initiate film growth

The atomization procedure is the first step in the spray pyrolysis deposition system. The idea is to generate droplets from a spray solution and send them, with some initial velocity, towards the substrate surface. Spray pyrolysis normally uses air blast, ultrasonic, or electrostatic techniques. The atomizers differ in resulting droplet size, rate of atomization, and the initial velocity of the droplets. The spraying time, volume of the sprayed solution, air pressure, distance
of the atomizer from the substrate, temperature of the pyrolysis reaction, and time of the solution aging are the various factors which influence the thickness and morphology of the deposited film.

**Figure 2.5:** Spray pyrolysis equipment

**2.3.5. Doctor-Blade method**

The doctor blade is a method in which excess paste/sol of the desired coating material is removed from the smooth non-engraved portions of the substrates using a sharp object such as blade, glass slide etc. (Fig. 2.6). The thickness of the coating layer (10–500 µm) is controlled by the gap between the sharp blade and the substrate. The film thickness depends on the surface energy of the substrate, the surface tension of the solution, the viscosity, and the meniscus of the
thin film. The thickness of the deposited layer is given as: $d = g c / \rho$, $d$ is the thickness, $g$ is the gap between the substrate and the blade, $c$ is the solid content (g/cm$^3$), and $\rho$ is the final density (g/cm$^3$) of the thin film. With respect to the shearing stress that is generated by the blade movement, the linear velocity need not be high.

Figure 2.6: Schematic diagram of Doctor-Blade method

2.4. Characterization methods

2.4.1. Stylus profilometer

A contact stylus profilometer (Dektak150, Veeco Inc.) was used to characterize the surface profiles of nano-structured films (Fig. 2.7). These measurements were used to compare the thickness of TiO$_2$ layers deposited by various techniques. The contact stylus profilometer works by electromechanically moving the sample under a diamond-tipped stylus. The test part sits on a high precision translation and rotation stage according to the translation speed, stylus force and scan length. As the stage moves across the sample, surface variations cause the stylus to be translated vertically. The resultant vertical motion of the stylus compresses a piezoelectric element which generates a fairly linear voltage response. The vertical resolution of this instrument is 1 Å. Computer algorithms are then used to convert these signals into height variation information.
2.4.2. Scanning electron microscopy (SEM)

The scanning electron microscopy was used to determine the average crystallite size and the surface morphology of the bulk titanium dioxide layers. It gives information about the grain evolution and grain size in the titanium dioxide layer. It also gives information about intergranular pores and their distribution of grains in the bulk samples. SEM micrographs of the titanium dioxide layer are obtained using scanning electron microscope. Fig 2.8 shows the schematic ray diagram of Scanning electron microscope. In this instrument, electrons emitted due to thermionic emission from a filament are accelerated using high accelerating potential typically between 0-50 kV and focused using magnetic field and electric field as fine beam. This focused beam is used to irradiate the sample. The secondary electrons emitted from the sample, are detected using a detector placed at a certain angle with respect to the sample.

The secondary electrons, backscattered electrons, auger electrons, characteristic X-rays and several other radiations are released from the specimen. Generally, the secondary electrons are collected by a detector, originating from the subsurface depth having range of several
angstroms. To avoid the charging effect due to the insulating behaviour of the ceramics, they were coated with a conducting layer of gold, thickness of about 100 Å by using the DC magnetron sputtering.

**Figure 2.8:** The schematic ray diagram of Scanning electron microscope

### 2.4.3. Atomic force microscopy (AFM)

Atomic force microscope (EasyScan2, Nanosurf) was used to characterize the surface of metallic films. Atomic force microscopy is a non-destructive technique, which uses a nanometer sized tip located at the free end of a cantilever, to probe the surface topography of samples [276]. A detector measures the cantilever deflection as the tip is scanned over the sample surface and these deflections are used to generate a map of the surface topography. A schematic diagram is shown in Fig. 2.9.
AFM operates by measuring attractive or repulsive forces between the cantilever tip and the sample. In its repulsive "contact" mode, the instrument’s tip makes a light contact with the sample. As a raster-scan drags the tip over the sample, a detection apparatus measures the vertical deflection of the cantilever, which indicates the local sample height. Thus, in contact mode, the AFM measures hard-sphere repulsion forces between the tip and sample. In non-contact mode, the AFM derives topographic images from measurements of attractive forces; the tip does not touch the sample. AFMs can achieve a resolution of 10 pm, and unlike electron microscopes, can image samples in air and under liquids [277].

**Figure 2.9**: Schematic diagram of the atomic force microscope (contact mode)

Apart from the flexibility of operating modes, the other most important advantage with AFM is that (unlike STM or SEM) AFM can image surfaces irrespective of its conducting or non-conducting nature. It can also provide three-dimensional images of the sample surface and in
that way the surface roughness can also be mapped. The sensitive detection in case of AFM is achieved by employing a laser beam to measure the deflection of the cantilever. The high flexibility of the cantilever ensures that the damage occurred on the sample surface is minimum. In order to have a low spring constant and high resonant frequency, the mass of the cantilever is kept extremely light. The sharpness of the AFM tip is very important because in combination with tip-sample interaction effects, this end radius generally limits the resolution of AFM. For an accurate positioning of tip and sample, piezoelectric material is used. Piezo-ceramics make it possible to create three-dimensional positioning devices of arbitrarily high precision. Presently, most of the scanning-probe microscopes use tri axis tube-shaped piezo-ceramics because they combine high resolution and large scan range. The mechanism of each axis movement is described below. Four electrodes cover the outer surface of the tube, while a single electrode covers the inner surface. Application of voltages to one or more of the electrodes causes the tube to bend or stretch, moving the sample in three dimensions. AFMs use force feedback network to regulate the force on samples. The presence of a feedback loop is one of the subtler differences between AFMs and older stylus-based instruments such as record players and stylus profilometers. The AFM not only measures the force on the sample but also regulates it, allowing acquisition of images at very low forces. The feedback loop consists of the tube scanner that controls the height of the entire sample; the cantilever and optical lever, which measures the local height of the sample and a feedback circuit that attempts to keep the cantilever deflection constant by adjusting the voltage applied to the scanner. The faster the feedback loop can correct deviations of the cantilever deflection, the faster the AFM can acquire images; therefore, a well-constructed feedback loop is essential to microscope performance. AFM feedback loops tend to have a bandwidth of about 10 kHz, resulting in image acquisition times of about one minute. The typical forces between tip and sample ranges from $10^{-11}$ to $10^{-6}$ N [278].

2.4.4. X-ray Diffraction (XRD)

XRD is the basic characterization technique for structural and phase analysis. Basically XRD is used for the following purposes:

I. Identification of the crystalline phases including lattice constants and crystal structure

II. Identification of the unknown phases
III. Determination of the preferred orientation of polycrystalline and crystalline samples

IV. Measurement of the stress and crystalline size of ceramics and thin films

The systematic diffraction of X-rays from different planes of the crystal makes XRD a powerful technique to study the crystalline materials. An XRD instrument measures the intensity of diffraction as a function of scan angle $2\theta$. These $2\theta$ values can be used for calculating the inter-planner spacing ‘$d$’ by Bragg’s diffraction equation;

$$2d \sin \theta = n \lambda$$  \hspace{1cm} (2.1)

where $n$ is the order of reflection, $\theta$ is the Braggs angle of diffraction and $\lambda$ is the wavelength of the source.

The structural characterization of the deposited TiO$_2$ thin films was done using the X-ray diffractometry. For this purpose, an X-ray diffractometer from PAN Analytical (model proexpert) was used. The source was Cu K$\alpha$ radiation having the wavelength of 1.54 Å from a copper anode that can yield a maximum power of 1.8 kW. The conventional diffractometers do not result in intense diffraction peaks in case of thin films due to the normal incidence of the beam. This results in dominating peaks from underlying substrate, which act as a source of noise. Using incident angle in the glancing range ($1^\circ$-$5^\circ$) ensures that the most diffracted X-rays emerge as the film contribution, rather than the substrate. In case of GAXRD, the film appears to be thicker to the incident beam than it actually is, and hence reduces signal from the substrate considerably while enhancing signal from the film.

Figure 2.10 shows the schematic diagram of X-ray optics in a glancing angle X-ray diffractometer. In this geometry, X-rays from the source is narrowed by the incident slit and strike the sample at an angle $\alpha$ very close to the surface. The divergence of the incident X-rays in the vertical direction becomes very limited by the use of divergence limiting soller slit. The height of the incident x rays at the sample position is limited by the incident height-limiting slit. Diffracted X-rays from the thin film sample pass through the receiving soller slit and also through a monochromator (graphite flat crystal), and finally fall on the detector, a scintillation counter. The incident angle is kept constant during the measurement. The sample rotates in a vertical plane to take care of the preferential orientation of the grains. The output from the detector goes to a computer, which then records the spectrum.
The inter-planer spacing (d) and full width at half maxima (FWHM) were calculated using the standard software provided by Philips. In the present studies, a glancing angle of 3° was chosen for all the thin film samples.

### 2.4.5. UV-Vis-NIR spectroscopy

Dual beam UV-Vis-NIR spectrophotometer (Perkin Elmer Lambda 750) has been employed for measuring the total transmittance and reflectance of thin films. The wavelength range available on this instrument is from 250 nm to 2500 nm. The light sources used in the instrument are tungsten and deuterium lamps. Resolution of the instrument is 0.05 nm in the UV-Vis region and 0.2 nm in NIR region. The wavelength accuracy of the instrument is ±0.08 nm in UV-Vis region, and ±0.3 nm in NIR region. The reflectance is measured with respect to the standard 2” diameter MgSO₄ coated Teflon disc and transmittance with respect to air medium.
The arrangement of various optical components of the spectrophotometer used in the present study is shown in Fig. 2.11. The radiation emitted by the sources passes through a monochromator where it is dispersed by gratings into its spectral components. As the grating is rotated, the dispersed spectrum is scanned across the monochromator exit slit. The dispersed beam is then split into two beams. Before entering into the sample and reference compartments, these components pass through attenuators. Then the beams after being scattered in the integrated sphere fall on the detectors (a photomultiplier for the ultraviolet and visible region and a thermostat regulated lead sulfide for NIR region).

![Schematic diagram of arrangement of different optical components of UV-Vis-NIR spectrophotometer](image)

**Figure 2.11:** Schematic diagram of arrangement of different optical components of UV-Vis-NIR spectrophotometer
2.4.6. Electrical characterization

2.4.6.1. Impedance measurements

Electrochemical Impedance Spectroscopy (EIS) is a technique extensively used for characterizing the electrical behavior of systems in which overall performance is determined by a number of strongly coupled processes, each taking place at a different rate. The most common and standard procedure in impedance measurements consists of applying a small sinusoidal voltage perturbation and monitoring the resulting current response of the system at the corresponding frequency. An electrochemical workstation (Model 600D, CH Instruments, USA) has been used for impedance measurements of fabricated devices (Fig. 2.12).

![Figure 2.12: Schematic representation of electrochemical workstation used for EIS of DSSC](image)

The single-frequency voltage perturbation is usually done at open-circuit conditions with magnitude $V_0$ of the modulation signal [279]:

$$V(t) = V_{oc} + V_0 \cos (\omega t) \quad (2.2)$$

The current response has the same period as the voltage perturbation but will be phase shifted by $\phi$:

$$I(t) = I_0 \cos (\omega t - \phi) \quad (2.3)$$

$V_0$ and $I_0$ are the amplitudes of the voltage and current signals, respectively, and $\omega$ is the radial frequency in radians per second.

The high frequency part of EIS spectrum contains information about transport and series resistance elements as well as dielectric contributions. The low frequency arc represents the
contribution of recombination in the solar cell, capacitance, resistance and lifetime values. From EIS, several parameters can be obtained, such as charge-transfer resistance at the CE, electron recombination resistance at the TiO2/dye/electrolyte interface as well as diffusion resistance in the electrolyte etc.

2.4.6.2. Capacitance-voltage measurements

Capacitance–voltage (C-V) measurement is an important tool to understand the material aspects of a semiconductor device. Generally capacitance is measured in the reverse bias (Mott-Schottky) condition to determine the potential difference between conduction band edge of TiO2 and redox potential of electrolyte (barrier potential, \( V_{bi} \)) and effective carrier concentration (\( N \)). For C-V measurements of DSSC, an electrochemical workstation (Model 600D, CH Instruments, USA) has been used.

The dependence of barrier potential and effective carrier concentration at the TiO2/dye/electrolyte interface capacitance (\( C \)) per unit area is given by [280, 281]:

\[
\frac{1}{\varepsilon} = \frac{2}{qK\varepsilon_0N} \left( V_{bi} - V - \frac{2k_BT_C}{q} \right) \tag{2.4}
\]

\[
\frac{d(1/\varepsilon)}{dV} = -\frac{2}{qK\varepsilon_0N} \tag{2.5}
\]

where \( q \) is the electron charge, \( K \) is the dielectric constant of TiO2, \( \varepsilon_0 \) is the permittivity of free space, \( k_B \) is Boltzmann’s constant, \( T_C \) is equal to 300 Kelvin and \( V \) represents applied potential.

2.4.6.3. Current-voltage measurements

The photovoltaic characteristic of DSSC is measured under AM1.5 solar simulator (Class AAA, PEC Inc., USA). The power of the simulated light was calibrated to be 100 mW/cm² by using a reference Si photodiode equipped with an IR cut-off filter. The current-voltage curve was obtained by applying an external bias to the cell and measuring the generated photocurrent with a digital source meter (Model U2722A, Agilent, USA) (Fig. 2.13). Current-voltage (I-V) characterization is very significant technique to study the non-linear response of the DSSC under dark and illuminated conditions.

The dye-sensitized solar cell device can be represented by an equivalent circuit (Fig. 2.14) commonly used for solar cells [282, 283].
The TiO$_2$/sensitizer/electrolyte interface is normally modeled as Schottky diode. The I-V equation of such a diode is given as [36, 283]:

$$I_D = I_t \left\{ \exp \left( \frac{q(V+I R_S)}{n k_B T_C} \right) - 1 \right\}$$

(2.6)
where, $I_D$ represents the “diode” current; $R_S$ represents series resistance, $I_i$ represents the saturation current, $n$ represents the ideality factor and $T_C$ represents the cell temperature.

The current-voltage equation for such a diode is given by:

$$I = I_{ph} - I_i \left\{ \exp \left( \frac{q(V+IR_S)}{nk_BT_C} \right) - 1 \right\} - \frac{(V + IR_S)}{R_{sh}}$$ (2.7)

In a DSSC the shunt resistance is normally much larger, so the simplified equation can be written as:

$$I = I_{ph} - I_i \left\{ \exp \left( \frac{q(V+IR_S)}{nk_BT_C} \right) - 1 \right\}$$ (2.8)

Short-circuit current ($I_{SC}$) and open-circuit voltage ($V_{OC}$) can be obtained using following conditions:

1. The current equals the short-circuit current when the applied bias is zero:

$$I_{SC} = I_{ph} - I_i \left\{ \exp \left( \frac{qI_{SC}R_S}{nk_BT_C} \right) - 1 \right\}$$ (2.9)

2. Under the open circuit conditions, no current is flowing through the cell and so the open-circuit voltage can be found from the equation given below:

$$V_{OC} = n \times \frac{nkbT_C}{q} \times \left\{ \ln \left( \frac{I_{ph}}{I_i} + 1 \right) \right\}$$ (2.10)

The power delivered from a solar cell is the product of the current at this potential times the voltage:

$$P(V) = I(V) \times V$$ (2.11)
Figure 2.15: Representation of the I-V and power curves (MPP is the maximum power point)

Figure 2.15 shows maximum power point at $V_{\text{max}}$. The fill-factor of the solar cell is calculated using the following equation:

$$FF = \frac{V_{\text{max}} \times I_{\text{max}}}{V_{\text{OC}} \times I_{SC}}$$  \hspace{1cm} (2.12)$$

The maximum power output of dye-sensitized solar cell is related to the $I_{SC}$ and $V_{OC}$ by following equation:

$$P_{\text{MAX}} = FF \times V_{OC} \times I_{SC}$$  \hspace{1cm} (2.13)$$

The values of $I_{SC}$, $V_{OC}$ and $FF$ can be determined from the I-V characteristics obtained experimentally.

The efficiency of the solar cell in relation with the $P_{\text{MAX}}$ is given by following equation:

$$\eta = \frac{P_{\text{MAX}}}{(A \times \lambda)}$$  \hspace{1cm} (2.14)$$

where, $A$ represents the area of the solar cell and $\lambda$ is the incident solar radiation (W/m$^2$).
3.1. Introduction

In recent years, dye-sensitized solar cells (DSSCs) based on nanocrystalline mesoporous TiO$_2$ films have attracted much attention as a potential low-cost alternative to single or polycrystalline p–n junction silicon solar cells. DSSCs can reach electrical energy conversion efficiencies $\approx 12\%$ [154, 284]. The traditional mesoporous TiO$_2$ electrode composed of the TiO$_2$ nanoparticles offer insufficient electron diffusion coefficient due to multiple trapping and de-trapping events occurring in the porous semiconductor grain boundaries of the TiO$_2$ nanoparticles and ultimately reduces the efficiency [285]. Electrodes based on aligned nanorods of TiO$_2$ have emerged as a potential candidate for the improvement of electron diffusion coefficient and the efficiency of DSSC due to their exceptional charge collection properties [285, 286]. Adachi group has shown high conversion efficiency of 7.29% using TiO$_2$ nanorods with lengths of 100-300 nm and diameters of 20-30 nm synthesized by hydrothermal process [286]. There exists wide literature on the modeling and experimental validation of DSSC [287-328]. But nanostructured TiO$_2$ electrode based DSSC is not fully explored for their dynamic behavior.

3.2. DC Modeling of TiO$_2$ based DSSC

The band-diagram of DSSC is given in Fig. 1.7 and the detailed working is discussed in chapter 1, section 1.8. Under a steady-state condition of illuminated DSSC, the electron injection from excited dye molecules, transport in the mesoporous semiconductor (TiO$_2$) thin film, and recombination with electrolyte at the TiO$_2$/electrolyte interface can be described by the following electron diffusion differential equation [322-324]:

$$D \frac{\partial^2 n(x)}{\partial x^2} - \frac{n(x) - n_0}{\tau} + \Phi_0 \alpha \exp(-\alpha x) = 0$$

(3.1)

where $n(x)$ is the excessive electron concentration at position $x$ inside the mesoporous TiO$_2$ thin layer; $n_0$ is the electron concentration under a dark condition ($n_0 = 10^{16}$ cm$^{-3}$) [287, 288]; $\tau$ is the
lifetime of conduction band free electrons; $\Phi_0$ is the incident irradiation intensity; $\alpha$ is the light absorption coefficient of the mesoporous TiO$_2$ thin layer; and $D$ is the electron diffusion coefficient. The effect due to transport of $I^-/I_3^-$ redox electrolyte is neglected because the pore sizes in DSSC are normally greater than or comparable to 14 nm [329]. In a steady state, trapping-detrapping in the electron transport can be neglected and hence the electron lifetime $\tau$ is assumed to be constant in a DSSC [322-324]. The general solution of Eq. (3.1) in terms of $J$-$V$ relationship, with short-circuit current and open-circuit voltage boundary conditions, can be expressed as below:

$$J = J_{ph} - J_0 \{ \exp(qV/mk_bT) - 1 \}$$  \hspace{1cm} (3.2)$$

where $J_{ph}$ is the photo-generated current density; $J_0$ is the reverse saturation current density; $q$ is the electron charge; $m$ is the ideality factor; $k_b$ is the Boltzmann constant; and $T$ is the absolute temperature. In the Eq. (3.2), the photo-generated and reverse saturation current densities can be expressed as below:

$$J_{ph} = \frac{q\Phi_0 L \alpha \left[ -L \alpha \cosh \left( \frac{d}{L} \right) + \sinh \left( \frac{d}{L} \right) + L \alpha \exp(-d\alpha) \right]}{A(1 - L^2\alpha^2) \cosh \left( \frac{d}{L} \right)}$$  \hspace{1cm} (3.3)$$

and,$$J_0 = \frac{q \Phi_0 L \alpha \sinh (d/L)}{AL \cosh (d/L)}$$  \hspace{1cm} (3.4)$$

where $L$ is the electron diffusion length equal to $\sqrt{D\tau}$; $d$ is the mesoporous TiO$_2$ layer thickness; and $A$ is the area of the DSSC.

Further, the light absorption coefficient $\alpha$ and the electron diffusion coefficient $D$ are related to the porosity $P$ of the mesoporous TiO$_2$ layer by following expressions [322]:

$$\alpha = 2.97 \times 10^4 P^2 \hspace{1cm} \text{for} \hspace{0.5cm} 0 \leq P < 0.41$$  \hspace{1cm} (3.5)$$

$$D = 1.69 \times 10^{-4}(-17.48 P^3 + 7.39 P^2 - 2.89 P + 2.15) \hspace{0.5cm} \text{for} \hspace{0.5cm} 0 \leq P < 0.41$$  \hspace{1cm} (3.6)$$
\[ \alpha = 2568 \left(1 - P\right)\left(P + 2.89\right) \quad \text{for} \quad 0.41 \leq P < 0.76 \quad (3.7) \]

\[ D = a \left|P - P_c\right|^{\mu} \quad \text{for} \quad 0.41 \leq P < 0.76 \quad (3.8) \]

where \( a \) is equal to \( 4 \times 10^{-4} \, \text{cm}^2 \, \text{s}^{-1} \); \( \mu \) is equal to 0.82; and critical porosity \( P_c \) is equal to 0.76. This model is used to predict current-voltage characteristics of TiO\textsubscript{2} nanoparticle based DSSC (Fig. 3.1).

For the nanorod based electrode (Fig. 3.2), the porosity is dependent on the diameter of nanorod and inter-rod distance as described by Eq. (3.9).

\[ P = \frac{2\pi w^2}{\sqrt{3} l^2} \quad (3.9) \]

where, \( w \) represents the diameter of nanorod and \( l \) represents center-to-center distance among nanorods.

**Figure 3.1**: Schematic diagram of TiO\textsubscript{2} nanoparticle-based dye-sensitized solar cell

The developed theoretical model is validated with TiberCAD software for both DSSC (based TiO\textsubscript{2} nanoparticle and nanorod) and experimental data available in the literature.
Figure 3.2: Schematic diagram of nanorod based dye-sensitized solar cell

3.2.1. Simulation

The one-dimensional (1-D) DSSC simulation is done using computer aided design software, called TiberCAD. The TiberCAD uses a theoretical model consisting of a set of drift-diffusion equations for the propagation of ions and electrons coupled with Poisson’s equation as fully described by Gagliardi et al. [321]. The simulation was performed using a 1-D model of DSSC. It assumes that the DSSC has two physical regions as shown in Fig. 3.3:

Region 1: Mesoporous TiO₂ layer, where light absorption, carrier generation and recombination take place

Region 2: Electrolyte region

Two boundary points represent the photo-anode (left) and the counter-electrode (right).
The above mentioned model is used for simulating the nano-particle based TiO$_2$ electrode as well as nanorod based TiO$_2$ electrode in TiberCAD by controlling simulation parameters. The simulation parameters are listed in Table 3.1.

### Table 3.1: Fitting parameters used in the simulation using TiberCAD software [321]

<table>
<thead>
<tr>
<th>Parameter (in TiberCAD)</th>
<th>Value (Nano-particle)</th>
<th>Value (Nanorod)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ layer thickness ($\mu$m)</td>
<td>7, 10</td>
<td>7, 10</td>
</tr>
<tr>
<td>Electron relaxation rate ($k_e$)</td>
<td>$10^4$ s$^{-1}$</td>
<td>$10^4$ s$^{-1}$</td>
</tr>
<tr>
<td>Electron mobility ($\mu_e$)</td>
<td>0.3 cm$^2$/V-s</td>
<td>0.6 cm$^2$/V-s</td>
</tr>
<tr>
<td>Iodide diffusion coefficient ($D_{I^-}$)</td>
<td>$8.5 \times 10^{-6}$ cm$^2$/s</td>
<td>$8.5 \times 10^{-6}$ cm$^2$/s</td>
</tr>
<tr>
<td>Triiodide diffusion coefficient ($D_{I^-}$)</td>
<td>$8.5 \times 10^{-6}$ cm$^2$/s</td>
<td>$8.5 \times 10^{-6}$ cm$^2$/s</td>
</tr>
<tr>
<td>Initial concentration of iodide ($\bar{n}_{I^-}$)</td>
<td>0.45 M</td>
<td>0.45 M</td>
</tr>
<tr>
<td>Initial concentration of triiodide ($\bar{n}_{I^-}$)</td>
<td>0.05 M</td>
<td>0.05 M</td>
</tr>
<tr>
<td>Recombination exponent ($\beta$)</td>
<td>0.7 (from [321])</td>
<td>0.8 (fitted value)</td>
</tr>
<tr>
<td>Trap exponent ($a$)</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Cell porosity ($\epsilon_p$)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

### 3.2.2. Validity of the reported model

A MATLAB code was written using a theoretical model presented in section 3.2.1. The simulation parameters used in MATLAB are listed in Table 3.2. The results were verified using one-dimensional DSSC model of TiberCAD software.

The results generated by the theoretical model agree well with the results of TiberCAD software as shown in Fig. 3.4 for the set of parameters listed in Table 3.1 and Table 3.2. The discussed theoretical model is also validated with the experimental results reported by Kang et al.
and is shown in Fig. 3.5. The simulation parameters for experimental validation are listed in Table 3.3.

Figure 3.4: Current-voltage characteristics of DSSC; A: for ~7 µm thick TiO₂ electrode and B: for ~10 µm thick TiO₂ electrode for nano-particle (NP) and nanorod (NR)
### Table 3.2: Simulation parameters used in MATLAB for the reported model

<table>
<thead>
<tr>
<th>Parameter (in MATLAB)</th>
<th>Value (Nanoparticle)</th>
<th>Value (Nanorod)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer thickness (µm), d</td>
<td>7, 10</td>
<td>7, 10</td>
<td>--</td>
</tr>
<tr>
<td>Proportionality constant for diffusivity to porosity (cm²/s), a</td>
<td>4 x 10⁻⁴</td>
<td>4 x 10⁻⁴</td>
<td>[322]</td>
</tr>
<tr>
<td>Power factor for diffusivity to porosity, µ</td>
<td>0.82</td>
<td>0.82</td>
<td>[322]</td>
</tr>
<tr>
<td>Critical Porosity, P&lt;sub&gt;C&lt;/sub&gt;</td>
<td>0.76</td>
<td>0.76</td>
<td>[322]</td>
</tr>
<tr>
<td>Carrier Lifetime (ms), τ</td>
<td>22</td>
<td>46</td>
<td>[285, 325]</td>
</tr>
<tr>
<td>Absolute temperature (K), T</td>
<td>300</td>
<td>300</td>
<td>--</td>
</tr>
<tr>
<td>Ideality factor, m</td>
<td>2.3</td>
<td>2.2</td>
<td>Fitted value</td>
</tr>
<tr>
<td>Porosity (Calculated value from the model)</td>
<td>0.5</td>
<td>0.5</td>
<td>Fitted value</td>
</tr>
</tbody>
</table>

**Figure 3.5:** Current-voltage characteristics of DSSC matched with the experimental data reported by Kang et al. [285]
Table 3.3: Simulation parameters used in MATLAB for experimental validation (rest of the parameters remain same as given in Table 3.2)

<table>
<thead>
<tr>
<th>Parameter (in MATLAB)</th>
<th>Value (Nanoparticle)</th>
<th>Value (Nanorod)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer thickness (µm), d</td>
<td>7.5</td>
<td>7.1</td>
<td>[285]</td>
</tr>
<tr>
<td>Ideality factor, m</td>
<td>3.7</td>
<td>3.7</td>
<td>Fitted value</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>55.9%</td>
<td>53.4%</td>
<td>[285]</td>
</tr>
</tbody>
</table>

The reported theoretical model generated data match well with experimentally reported current-voltage characteristics of a nanoparticle (NP) and nanorod (NR) based dye sensitized solar cell as shown in Fig. 3.5. This confirms the validity of the theoretical model presented here.

3.2.3. Results and Discussion

The considerable shift in the current-voltage curve of nanorod as compared to the current-voltage curve of nanoparticle may be attributed to reduced intercrystalline contacts between grain boundaries and stretched grown structure to the specific directionality made a slightly favorable contribution to the electron transport [285]. There may be several reasons for improvement of output power from the nanorod based DSSC:

1. Improved carrier lifetime by the degraded charge recombination through experiencing the less frequent trapping/detrapping events
2. Low recombination rate as demonstrated by the parameters listed in Table 3.1
3. Slightly improved electron transport due to the necking of grain boundaries and increased average crystallite size

The dependence of short-circuit current density ($J_{SC}$) on the diameter of the nanorod is shown in the Fig. 3.6. The short-circuit current density increases with an increase in the nanorod diameter up to 80 nm and afterwards falls drastically. The observed effect may be attributed to the variation in the porosity of the TiO$_2$ electrode layer, which decreases with increasing diameter as shown in the Fig. 3.7. The increase in current density with increasing nanorod diameter may be attributed to decrease in the grain boundaries and increase in grain size. But the control parameter
is the porosity of the TiO$_2$ electrode layer which decreases with increasing diameters of the nanorod (Fig. 3.7).

**Figure 3.6:** The dependence of the current-density on the nanorod diameter for inter-rod separation of 200 nm

From these results it is evident that the nanorod diameter plays a crucial role in the improvement of $J_{SC}$ of dye-sensitized solar cell. The nanorods of diameter from 65 nm to 90 nm with porosity range from 0.43 to 0.66 would result in better performing DSSC as observed in Fig. 3.6 and Fig. 3.7.
3.3. AC Modeling of DSSC

3.3.1. Prediction of I-V curve of DSSC

An operating DSSC is principally governed by the relative kinetic rates of several charge transfer steps. The charge transfer taking place from excited dye to TiO$_2$ nanoparticle, from electrolyte to the dye and from TiO$_2$ to the load terminal plays very critical role in the performance of DSSC. Thus, it is very important to understand all the electronic processes taking place at the TiO$_2$ nanoparticles level, as well as the dynamics of charge separation and charge transport at the metal/oxide interface.

Since in DSSCs, the function of light absorption is separated from the charge carrier transport, the dye should have a broad absorption spectrum in order to harvest the maximum amount of solar radiation. The excited-state of the dye must energetically lie above the conduction band edge of the TiO$_2$ nanoparticles to assure fast electron injection, before it can fall back to its ground state [328]. On the other hand, the oxidized dye must have a higher positive potential than the redox-couple in the electrolyte. Thus, the regeneration of the dye by the redox

![Figure 3.7: Variation in porosity with respect to the nanorod diameter](image)
The electrolyte must be extremely fast compared with the recombination of the injected electrons with the oxidized dye.

The redox electrolyte is responsible for the dye regeneration, becoming oxidized by electron injection to the TiO$_2$ conduction band. Moreover, the electrolyte conducts the positive charges (holes) to the counter-electrode, where the redox-couple itself is regenerated. As the open-circuit voltage of the system corresponds to the difference between the redox potential of the electrolyte and the TiO$_2$ Fermi level, the redox potential must be as positive as possible in order to assure high open-circuit voltages and to overcome the problem related to slow charge-transfer reaction at the counter-electrode, a platinum-based catalyst must be employed. On the other hand, the voltage at the semiconductor/dye interface should be high, since the dark current caused by the electron back transfer to the electrolyte decrease the number of electrons available for photocurrent.

A standard DSSC consists of three interfaces formed by FTO/TiO$_2$, TiO$_2$/dye/electrolyte, and electrolyte/Pt-FTO represented by an equivalent circuit shown in Fig. 3.8 [330]. The interfacial charge transfer at the TiO$_2$/dye/electrolyte is characterized by a rectifying diode $D_r$ and a double-layer capacitance $C_i$. A recombination diode $D_r$ with an ideality factor, $m$ is employed to denote the interfacial charge recombination losses to both the dye cation and the redox electrolyte. A shunt resistance $R_{sh}$ takes into account all parallel resistive losses across the photovoltaic device including leakage current. The photo generated current $I_{ph}$ is in parallel with the rectifying diode. An inductive recombination pathway on account of charge-transfer current [330] is incorporated into the circuit, consisting of a recombination resistance ($R_{rec}$) in series with an inductor (L). The charge-transfer resistance and interfacial capacitance at the FTO electrode and electrolyte/Pt-FTO interface are characterized by $R_E$ and $C_E$, and $R_{CE}$ and $C_{CE}$, respectively. The Nernst diffusion of the carrier transport by ions within the electrolyte is denoted by the Warburg impedance (W). A resistance element $R_S$ represents the bulk and contact resistive losses present in a DSSC, such as the sheet resistance of the FTO glass.
Figure 3.8: The equivalent circuit of DSSC

The current-voltage terminal equation with short-circuit current and open-circuit voltage boundary conditions; can be expressed as below [330]:

\[ I = I_{ph} - I_i \left\{ \exp \left( \frac{q(V+IZ)}{nk_BT_C} \right) - 1 \right\} - I_r \left\{ \exp \left( \frac{q(V+IZ)}{m_k_BT_C} \right) - 1 \right\} - (V +IZ)(j\omega C_i + 1/R_{sh}) \]  
(3.10)

\[ I_{ph} = [I_{SC} + K_1(T_C - T_{Ref})] \lambda \]  
(3.11)

\[ I_{SC} = \frac{[1-r(\lambda)]q\Phi_o L_0[-L_n \alpha \cosh \left( \frac{d}{l_n} \right) + \sinh \left( \frac{d}{l_n} \right)] + L_n \alpha \exp(-d\alpha)}{A(1-L_n^2\alpha^2) \cosh \left( \frac{d}{l_n} \right)} \]  
(3.12)

\[ Z = \frac{1}{R_{rec} + j\omega L_{rec}} + \frac{1}{j\omega C + j\omega + 1/R_{CE}} + W + R_S \]  
(3.13)

\[ Z_S = \frac{1}{j\omega C + 1/R_E} + \frac{1}{j\omega C + 1/R_{CE}} + W + R_S \]  
(3.14)

\[ W = \sigma \omega^{-\frac{1}{2}}(1 - j) \]  
(3.15)

where \( I_{ph} \) is the photo-generated current, \( I_i \) and \( I_r \) are the saturation current density of the rectifying and recombination diodes, respectively, \( n \) and \( m \) represent diode ideality factors, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( T_C \) is the cell temperature and \( T_{Ref} \) is the reference temperature (\( \approx 298.14 \) K), \( q \) is the electron charge, \( V \) is the voltage, \( R_{sh} \) represents shunt resistance, \( Z \) is the complex impedance, \( q \) is the electron charge, \( \omega \) is the angular frequency, \( \sigma \) is the Warburg coefficient, \( L_n \) is the electron diffusion length equal to \( \sqrt{D\tau} \).
The photocurrent density \( I_{ph} \) mainly depends on the solar insolation and on the operating temperature of the cell. The saturation current of a solar cell varies with the cell temperature, which is described by Eq. (3.20) and Eq. (3.21) \[153, 331\]:

\[
I_i = I_{RS1} \left( \frac{T_C}{T_{Ref}} \right)^3 \exp \left[ \frac{qE_g \left( \frac{1}{T_{Ref}} - \frac{1}{T_C} \right)}{nk_B} \right] \quad (3.20)
\]

\[
I_r = I_{RS2} \left( \frac{T_C}{T_{Ref}} \right)^{3/2} \exp \left[ \frac{qE_g \left( \frac{1}{T_{Ref}} - \frac{1}{T_C} \right)}{mk_B} \right] \quad (3.21)
\]

where, \( E_g \) represents the band-gap of the N719 dye molecule (\( \approx 1.6 \) eV). The reverse saturation current of the cell at a reference temperature depends on the open-circuit voltage \( V_{OC} \) and can be approximately obtained by following equation as given by Tripathi et al. \[331\] and Tsai et al. \[332\]:

\[
I_{RS1} = I_{SC}/\left[ \exp(qV_{OC}/k_BT_C) - 1 \right] \quad (3.22)
\]

The value of \( I_{RS2} \) is approximated as:

\[
I_{RS2} = I_{SC}/\left[ \exp(qV_{OC}/k_BT_C) - 1 \right] \quad (3.23)
\]

### 3.3.2. Prediction of dynamic resistance of DSSC

Due to the nonlinear I-V characteristic curve of the DSSCs, it is difficult to analyze and determine their output impedance, i.e., dynamic resistance. It is necessary to develop an efficient method to determine the dynamic resistance that corresponds to maximum power point (MPP) of DSSC. Being the dynamic quantity, the dynamic resistance is determined by the derivative of the I-V characteristics of the cell and is defined as the change in voltage divide by change in current \( (dV_m/dI_m) \) at MPP. In addition to this, the dynamic resistance is composed of series resistance and shunt resistance. A DSSC mainly consists of three types of resistances: series resistance \( R_s \), shunt resistance \( R_{sh} \) and dynamic resistance \( R_d \) as shown in Fig. 3.9. The series resistance \( R_s \), can be determined by various illumination conditions such as dark, constant illumination and varying illumination and they yield different results \[333\]. Practically, \( R_s \) is determined by using two different illumination levels, the so-called two-curve method. Shunts resistance, \( R_{sh} \), can be obtained from only one illuminated I-V curve, or single curve method. The output impedance of
solar PV module, i.e., dynamic resistance is usually composed of the series resistance and shunt resistance.

Using this method the dynamic resistance of the DSSC can be determined from single I-V characteristic curve under illumination. The model of the dynamic resistance with the combination of the finite series resistance and shunt resistance is also taken into consideration. Through the developed model, the effect of light intensity and temperature on the I-V characteristics and dynamic resistance of the DSSC is studied.

Figure 3.9: The components of resistance offered by DSSC

The terminal equation for current and voltage of the DSSC based on two-diode model (Eq. (3.11)) can be modified under the static condition ($\omega \approx 0$) as given below [153, 330]:

$$I = I_{ph} - I_r \left\{ \exp \left( \frac{q(V+IZ)}{n k_B T_c} \right) - 1 \right\} - I_T \left\{ \exp \left( \frac{q(V+IZ)}{m k_B T_c} \right) - 1 \right\} - \left( \frac{V +IZ}{R_{sh}} \right)$$

(3.24)

Eq. (3.24) is rearranged and the modified equation given by,
\[ I_{ph} + I_i + I_r - I = I_i \exp \left( \frac{q(V+IZ)}{nk_BT_C} \right) + I_r \exp \left( \frac{q(V+IZ)}{nk_BT_C} \right) \]  \hspace{1cm} (3.25)

In order to estimate the dynamic resistance Eq. (3.24) is subjected to following boundary conditions:

(i) \( 0 < V < V_m \) and \( I_m < I < I_{SC} \)

(ii) \( V_m < V < V_{OC} \) and \( 0 < I < I_m \)

For first boundary condition, \( I_r \gg I_i \), so the Eq. (3.25) can be rearranged as:

\[
\frac{q(V+IZ)}{nk_BT_C} = \ln \frac{R_{sh}[I_{ph} + I_i + I_r - I] - IZ}{R_{sh}/r} \] \hspace{1cm} (3.26)

From Eq. (3.26), the voltage across a load at one illumination level is given as:

\[
V = \frac{nk_BT_C}{q} \times \ln \frac{R_{sh}[I_{ph} + I_i + I_r - I] - IZ}{R_{sh}/r} - IZ \] \hspace{1cm} (3.27)

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

\[
V_1 = \frac{nk_BT_C}{q} \times \ln \frac{R_{sh}[I_{ph} + I_i + I_r - I_1] - I_1Z}{R_{sh}/r} - I_1Z \] \hspace{1cm} (3.28)

\[
V_m = \frac{nk_BT_C}{q} \times \ln \frac{R_{sh}[I_{ph} + I_i + I_r - I_m] - I_mZ}{R_{sh}/r} - I_mZ \] \hspace{1cm} (3.29)

For second boundary condition, \( I_r \ll I_i \), so the Eq. (3.25) can be rearranged as:

\[
\frac{q(V+IZ)}{nk_BT_C} = \ln \frac{R_{sh}[I_{ph} + I_i + I_r - I] - IZ}{R_{sh}/i} \] \hspace{1cm} (3.30)

From Eq. (3.30), the voltage across a load at one illumination level is given as:

\[
V = \frac{nk_BT_C}{q} \times \ln \frac{R_{sh}[I_{ph} + I_i + I_r - I] - IZ}{R_{sh}/i} - IZ \] \hspace{1cm} (3.31)

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:

\[
V_m = \frac{nk_BT_C}{q} \times \ln \frac{R_{sh}[I_{ph} + I_i + I_r - I_m] - I_mZ}{R_{sh}/r} - I_mZ \] \hspace{1cm} (3.32)
\[ V_2 = \frac{n k_B T_C}{q} \times \ln \frac{R_{sh}[I_{ph}+I_i+I_r-I_2]-I_2Z}{R_{sh}I_r} - I_2Z \]  

(3.33)

From Eq. (3.28) to Eq. (3.33), the Z can be rewritten as:

\[ Z = \frac{V_1-V_2}{I_2-I_1} \frac{(m-n)k_B T_C}{q} \ln \frac{R_{sh}[I_{ph}+I_i+I_r-1_2]-I_2Z}{R_{sh}[I_{ph}+I_i+I_r-1_2]-I_2Z} \] 

(3.34)

Eq. (3.34) can be simplified as a shunt resistance is normally much greater than series impedance Z. Thus \( R_{sh}(I_{ph} + I_i + I_r - I_2) \gg I_2Z \) and \( R_{sh}(I_{ph} + I_i + I_r - I_2) \gg I_2Z \). Therefore,

\[ Z = \frac{V_1-V_2}{I_2-I_1} \frac{(m-n)k_B T_C}{q} \ln \frac{I_{ph}+I_i+I_r-I_2}{I_{ph}+I_i+I_r-I_2} \] 

(3.35)

The first term of Eq. (3.35) 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.

For the open circuit condition and short-circuit conditions DSSC, following two expressions are given using the slope of one I-V characteristics at the points \((V_{OC}, 0) \) and \((0, I_{SC}) \) by

\[ R_{s0} = -\left( \frac{dI}{dV} \bigg|_{V=V_{OC}} \right)^{-1} \]  

(3.36)

and \[ R_{sh0} = -\left( \frac{dI}{dV} \bigg|_{I=I_{SC}} \right)^{-1} \]  

(3.37)

respectively. The dynamic resistance increases with the increase in temperature because of marginal increase in short-circuit current [334-336]. Based on the theoretical model described above, the DSSC is simulated using MATLAB/Simulink.

3.3.3. Validation and analysis of developed model

3.3.3.1. Current-voltage characterization

Current-voltage (I-V) characterization is very significant technique to study the non-linear response of the DSSC under dark and illuminated conditions. The simulated I-V characteristic of DSSC was experimentally validated by comparison with data from Grätzel [337] as shown in Fig. 3.10.
Figure 3.10: Simulated I-V curve matching well with the reported experimental data [337]

The input data used for simulation purposes are compiled in Table 3.4.

<table>
<thead>
<tr>
<th>$I_{ph}$ (mA/cm²)</th>
<th>$I_i$ (mA/cm²)</th>
<th>$I_r$ (mA/cm²)</th>
<th>$C_i$ (F)</th>
<th>$R_{sh}$ (Ω)</th>
<th>$R_{rec}$ (Ω)</th>
<th>$R_E$ (Ω)</th>
<th>$C_E$ (mF)</th>
<th>$R_{CE}$ (Ω)</th>
<th>$C_{CE}$ (μF)</th>
<th>$\sigma$ (Ω s$^{-1/2}$)</th>
<th>$R_S$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16.9</td>
<td>$0.4 \times 10^{10}$</td>
<td>$1.4 \times 10^{10}$</td>
<td>10</td>
<td>3000</td>
<td>4.2</td>
<td>21.7</td>
<td>0.8</td>
<td>9.8</td>
<td>19</td>
<td>4.2</td>
<td>12.6</td>
</tr>
</tbody>
</table>

It is evident from Fig. 3.10 that the outlined model agrees quite well with the experimental data. The reported cell’s efficiency of 11.04% ($J_{SC} = 16.9$ mA/cm²; $V_{OC} = 862$ mV; $P_{MAX} = 11.04$ mW; $R_S = 12.6$ Ω) [337] is in straight agreement with the simulated parameters of the DSSC having efficiency of 10.85% ($J_{SC} = 16.9$ mA/cm²; $V_{OC} = 862$ mV; $P_{MAX} = 10.85$ mW; $R_S = 10.85$ Ω). The experimental and simulated I-V curves were fitted by means of the parameters $R_S$, $R_{sh}$, $D_i$ and $D_r$. 

73
The curve at 0.65 sun and 0.1 sun were subsequently calculated using the same parameter as at 1 sun, by only changing the light intensity in the simulation (i.e., the recombination constant and the quantum injection yield are taken to be independent of light intensity). It can be seen that short-circuit current, maximum power point and the open circuit voltage are in general agreement with the experimental results.

### 3.3.3.2. Electrochemical impedance spectroscopy

In the Nyquist plots, the respective electrochemical steps with different time constants are represented by the semicircles as shown in Fig. 3.11. Three semicircles correspond to three interfaces formed by FTO/TiO$_2$, TiO$_2$/dye/electrolyte and electrolyte/Pt-FTO [337-339]. The triiodide diffusion was obtained by fitting the experimental EIS spectra under illumination to an appropriate electrical analogue [282, 340]. The diffusion of I$_3^-$ in the electrolyte is usually well described by Nernst diffusion impedance, characterized by Warburg parameter and a characteristic diffusion time constant [341, 342]. Due to excess of I$^-$ ions compared to I$_3^-$, the former does not contribute to the diffusion impedance [343].

![Figure 3.11: The EIS of simulated DSSC matches well with reported data [344]](image)

---

74
The low-frequency semi arc of 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 3.4. The values of I_i and I_r are found to be of the orders of 10^{-15} and 10^{-10} A/cm^2, respectively. The inductor L is 10–100 H [344]. The double-layer capacitance C_i is determined to be of the order of 10 F. The large capacitance value at the TiO_2/dye/electrolyte interface (C_i) is likely to 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, \( C_i = (R_{ct} \omega_{max})^{-1} \) [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.

3.3.4. Results and discussion

3.3.4.1. Effect of illumination on steady and dynamic parameters

The model proposed in section 3.3 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 DSSC are estimated under STC conditions. The simulated current-voltage characteristics of the DSSC are shown in Fig. 3.12 as a function of incident illumination at constant cell temperature. The increase in radiation intensity increases the number of photons striking the DSSC, resulting in enhanced dye excitation and electron transfer in the TiO_2 conduction band, and consequently in a larger photocurrent.

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 3.5. From the data given in Table 3.5, the series resistance, R_S shows a decreasing trend continuously with increase in the intensity of illumination.
Table 3.5: Effect of illumination on steady state and dynamic parameters of DSSC at 298.14 K

<table>
<thead>
<tr>
<th>Illumination (W/m²)</th>
<th>I_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>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>3.4</td>
<td>804.7</td>
<td>2.0</td>
<td>38.28</td>
<td>619.21</td>
<td>10.00</td>
</tr>
<tr>
<td>400</td>
<td>6.8</td>
<td>829.5</td>
<td>4.3</td>
<td>18.52</td>
<td>306.55</td>
<td>10.75</td>
</tr>
<tr>
<td>600</td>
<td>10.1</td>
<td>843.7</td>
<td>6.6</td>
<td>12.4</td>
<td>148.94</td>
<td>11.00</td>
</tr>
<tr>
<td>800</td>
<td>13.5</td>
<td>853.6</td>
<td>8.8</td>
<td>9.66</td>
<td>90.34</td>
<td>11.00</td>
</tr>
</tbody>
</table>

The calculated DSSC dynamic resistance values show a strong dependence on solar irradiation, which is similar to the trend observed in silicon solar cells [346]. The decrease in dynamic resistance with increase in solar radiation is attributed to a decreased R_S value. This is primarily caused by the logarithmic increase in V_OC and a linear increase in DSSC photocurrent with increasing illumination. The linear boost in I_SC is attributed to the increased dye-photon interaction and to the enhanced number of carriers injected from the excited dye molecules to the conduction band of TiO₂ electrode. A logarithmic dependence of V_OC on the illumination is observed in the DSSC and shown in Fig. 3.12. The dependence of V_OC on the illumination (λ) is given by [347]:

$$V_{OC} \alpha k_B T_c \frac{n^2}{q} \ln (\lambda) \quad (3.38)$$

The open-circuit voltage, V_OC is dependent on the saturation current density of the recombination diode (as described in section 3.3). From this study it is evident that the saturation current density of the recombination diode (I_r) is independent of the illumination intensity. This is mainly due to the insignificant change in magnitude of transport recombination, which governs the electron transport process occurring either in TiO₂ nanoparticle interfaces or at the electrode-electrolyte interface [348].
3.3.4.2. Effect of DSSC cell temperature on steady and dynamic parameters

Figure 3.13 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 3.6. 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 $J_{SC}$.

The small increase in $J_{SC}$ 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 3.13 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. As the temperature increases, the band gap of TiO$_2$ electrode decreases, which results in smaller difference between the redox potential of the electrolyte and the TiO$_2$ Fermi level, hence a reduced $V_{OC}$. A similar
decrease in $V_{OC}$ with increase in temperature of DSSC’s has been reported elsewhere [348]. Another significant factor which governs the decrease in $V_{OC}$ is the charge transfer and recombination which occurs at the dye-electrode interface, electrolyte-dye interface and electrolyte-counterelectrode interface.

Figure 3.13: The effect of cell temperature on the I-V curve of DSSC

Table 3.6: Effect of temperature on steady state and dynamic parameters of DSSC at 800 W/m$^2$

<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>$R_s$ (Ω)</th>
<th>$R_d$ (Ω)</th>
<th>Efficiency $\eta$ (%)</th>
<th>$I_r$ (A/cm$^2$)</th>
<th>$I_i$ (A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>13.5</td>
<td>853.6</td>
<td>8.8</td>
<td>9.66</td>
<td>90.34</td>
<td>11.00</td>
<td>$3.22 \times 10^{-7}$</td>
<td>$1.04 \times 10^{-13}$</td>
</tr>
<tr>
<td>303</td>
<td>13.5</td>
<td>827.4</td>
<td>8.5</td>
<td>10.05</td>
<td>96.77</td>
<td>10.62</td>
<td>$5.84 \times 10^{-7}$</td>
<td>$3.41 \times 10^{-13}$</td>
</tr>
<tr>
<td>308</td>
<td>13.6</td>
<td>801.2</td>
<td>8.1</td>
<td>10.45</td>
<td>102.95</td>
<td>10.12</td>
<td>$1.04 \times 10^{-6}$</td>
<td>$1.08 \times 10^{-12}$</td>
</tr>
<tr>
<td>313</td>
<td>13.6</td>
<td>774.9</td>
<td>7.8</td>
<td>10.88</td>
<td>108.64</td>
<td>9.75</td>
<td>$1.82 \times 10^{-6}$</td>
<td>$3.31 \times 10^{-12}$</td>
</tr>
</tbody>
</table>
The influence of above mentioned parameters on the overall conversion efficiency has also been simulated. The saturation current of rectifying diode \( (I_r) \) and saturation current of recombination diode \( (I_r) \), responsible for the transfer and recombination losses have a major influence on the overall conversion efficiency. Figure 3.14 show that the \( I_r \) plays a critical role in deciding the performance of the DSSC. It is important to mention here that the saturation current \( (I_r) \) for the recombination diode \( (D_r) \) is mainly dependent on the cell temperature (as described in section 3.3). As the temperature increases, \( I_r \) increases, which contributes to a further decline in DSSC output performance (Fig. 3.14). The performance of DSSC solar cell can also be correlated with their series and shunt resistance. Practically, the series resistance effect is more prominent for the degradation of I-V characteristics of DSSC. With the increase in DSSC working temperature, a higher series resistance offer greater power loss equivalent to \( I^2R_s \), thus reduce efficiency and also shifts maximum power point towards lower value. Recombination kinetics in the range of \( I_{SC} \) to the current at maximum power point \( (I_{MAX}) \) is dependent on shunt resistance. A higher shunt resistance and lower series resistance is needed.

![Figure 3.14: Influence of saturation current \( I_r \) on the electrical performance of DSSC](image)

Figure 3.14: Influence of saturation current \( I_r \) on the electrical performance of DSSC
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. 3.14).

3.4. Conclusions

In this chapter modeling and simulation is done to explore the effect of various parameters on the electrical performance of TiO$_2$ nanoparticle/nanorod based dye-sensitized solar cells. The model could be validated by simulation software TiberCAD and the experimental results available in the literature. The results show that the porosity decreases with increasing diameter of nanorod for a fixed value of inter-rod separation. The short-circuit current density can be improved by optimizing the nanorod diameter. From this study it is observed that the nanorods of diameter from 65 nm to 90 nm with porosity range from 0.43 to 0.66 would result in best performing DSSC. Further, The steady-state current–voltage curve and dynamic response of a DSSC is mathematically modeled based on the electrical equivalent circuit. The effect of temperature and illumination on the steady state and dynamic parameters of dye-sensitized solar cells are studied. It is found that the dynamic resistance of DSSC decreases from 619.21 Ω to 90.34 Ω with an increase in illumination level from 200 W/m$^2$ to 800 W/m$^2$. A positive temperature coefficient of dynamic resistance is observed. The interfacial charge transfer and recombination losses at the oxide/dye/electrolyte interface are found to be the most influential factor in the overall conversion efficiency and included in the mathematical model. The saturation current of rectifying diode and saturation current of recombination diode are responsible for the transfer recombination losses and have major influence on the overall conversion efficiency.