Chapter 3
Modeling and Simulation of Dye-Sensitized Solar Cell

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 detrapping 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:

$$J = J_{ph} - J_0 \{ \exp(qV/mk_BT) - 1 \}$$  

(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:

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

(3.3)

and, $J_0 = q \Phi_0 L \alpha \sinh \left( \frac{d}{L} \right)/AL \cosh \left( \frac{d}{L} \right)$  

(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]:

$$\alpha = 2.97 \times 10^4 P^2 \quad \text{for} \quad 0 \leq P < 0.41$$  

(3.5)

$$D = 1.69 \times 10^{-4}(-17.48 P^3 + 7.39 P^2 - 2.89 P + 2.15) \quad \text{for} \quad 0 \leq P < 0.41$$  

(3.6)
\[ \alpha = 2568 \, (1 - P)(P + 2.89) \quad \text{for} \quad 0.41 \leq P < 0.76 \]  
(3.7)

\[ D = a \, |P - P_c|^\mu \quad \text{for} \quad 0.41 \leq P < 0.76 \]  
(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\(_2\) 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).

\[ P = \frac{2\pi w^2}{\sqrt{3} l^2} \]  
(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\(_2\) nanoparticle-based dye-sensitized solar cell

The developed theoretical model is validated with TiberCAD software for both DSSC (based TiO\(_2\) 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 (µm)</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 ($D_{I_3^-}$)</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 ($\bar{n}_{I_3^-}$)</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 ($\alpha$)</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Cell porosity ($\varepsilon_p$)</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.
[270] 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 (Nano-particle)</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_c</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](image)

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
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$_i$ 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]:

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

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

\[ I_{SC} = \frac{(1 - r(\lambda)) q \Phi_0 L_0 \left( 1 - L_n \alpha \cosh \left( \frac{d}{L_n} \right) + \sinh \left( \frac{d}{L_n} \right) + L_n \alpha \exp(-d\alpha) \right)}{A(1 - L_n^2 \alpha^2) \cosh \left( \frac{d}{L_n} \right)} \]  
(3.12)

\[ Z = \frac{1}{R_{rec} + j\omega L} + \frac{1}{j\omega C_{in} + 1/R_{sh}} \]  
(3.13)

\[ Z_S = \frac{1}{j\omega C_{in} + 1/R_{sh}} + \frac{1}{j\omega C_{CE} + 1/R_{CE}} + W + R_S \]  
(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 \( \sqrt{D_t} \).
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]:

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

(3.20)

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

(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]:

\[
I_{RS1} = \frac{I_{SC}}{\exp(qV_{OC}/k_B nT_C) - 1}
\]  

(3.22)

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

\[
I_{RS2} = \frac{I_{SC}}{\exp(qV_{OC}/k_B mT_C) - 1}
\]  

(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 (ω ≈ 0) as given below [153, 330]:

\[
I = I_{ph} - I_t \left\{ \exp \left( \frac{q(V+IZ)}{nk_B T_C} \right) - 1 \right\} - I_r \left\{ \exp \left( \frac{q(V+IZ)}{nk_B T_C} - 1 \right) - \left( \frac{V+IZ}{R_{sh}} \right) \right\}
\]

(3.24)

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

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

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

\[ V = \frac{mk_BT_C}{q} \times \ln \frac{R_{sh}[I_{ph}+I_i+I_r-I] - IZ}{R_{sh}I_r} - IZ \]  \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:

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

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

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

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

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

\[ V = \frac{mk_BT_C}{q} \times \ln \frac{R_{sh}[I_{ph}+I_i+I_r-I] - IZ}{R_{sh}I_i} - IZ \]  \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:

\[ V_m = \frac{mk_BT_C}{q} \times \ln \frac{R_{sh}[I_{ph}+I_i+I_r-I_m] - I_mZ}{R_{sh}I_r} - I_mZ \]  \hspace{1cm} (3.32)
\[ V_2 = \frac{n k_b T C}{q} \times \ln \frac{R_{sh}[I_{ph} + I_i + I_r - I_2]}{R_{sh} I_r} - I_2 Z \]  

(3.33)

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

\[ Z = \frac{V_1 - V_2}{I_2 - I_1} \frac{(m - n) k_b T C}{q} \times \ln \frac{R_{sh}[I_{ph} + I_i + I_r - I_2]}{R_{sh} I_r} \frac{I_1 Z}{I_2 Z} \]  

(3.34)

Eq. (3.34) can be simplified as a shunt resistance is normally much greater than series impedance Z. Thus \( R_{sh} \frac{I_{ph} + I_i + I_r - I_2}{I_1 Z} >> I_2 Z \) and \( R_{sh} \frac{I_{ph} + I_i + I_r - I_2}{I_2 Z} >> I_2 Z \). Therefore,

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

(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

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

(3.36)

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

(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 3.4: Values of model parameters used in simulated I-V curves and Nyquist plots [330]

<table>
<thead>
<tr>
<th>$I_{ph}$ (mA/cm$^2$)</th>
<th>$I_i$ (mA/cm$^2$)</th>
<th>$I_r$ (mA/cm$^2$)</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×$10^{-16}$</td>
<td>1.4×$10^{-10}$</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/cm$^2$; $V_{OC} = 862$ 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/cm$^2$; $V_{OC} = 862$ 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 $D_r$. 

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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 diffusivity 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-url)
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_{phs}, 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, (\eta) (%)</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 TiO\(_2\) 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 (\(\lambda\)) is given by [347]:

\[
V_{OC} \propto \frac{k_BT_{CE}}{q} \ln (\lambda) \tag{3.38}
\]

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 TiO\(_2\) 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/m²

<table>
<thead>
<tr>
<th>Temperature (K)</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 (%)</th>
<th>$I_r$ (A/cm²)</th>
<th>$I_l$ (A/cm²)</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>3.22×10⁻⁷</td>
<td>1.04×10⁻¹³</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>5.84×10⁻⁷</td>
<td>3.41×10⁻¹³</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>1.04×10⁻⁶</td>
<td>1.08×10⁻¹²</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>1.82×10⁻⁶</td>
<td>3.31×10⁻¹²</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
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 $\Omega$ to 90.34 $\Omega$ 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.