DYE SENSITIZED SOLAR CELL: PARAMETERS CALCULATION AND MODEL INTEGRATION

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Abstract-- This article proposes an accurate approach to calculate the internal parameters of a dye sensitized solar cell DSSC (L, α, m, D, n_0, τ). This approach is based on the electron diffusion differential model and the values of the short circuit current density J_{sc}, the open circuit voltage V_{oc}, and the current density and the voltage at the maximum power point i.e. J_{mp} and V_{mp}, respectively.

Assuming, that the charge transfer at the counter electrode is potential controlled, the Butler-Volmer equation is adequately integrated with both the electron diffusion differential model, and the Schottky barrier model to account for the interfacial effect at counter electrode/electrolyte and TiO_2/TCO interfaces on the J-V characteristics. Some parametric analyses were conducted to study the effect of temperature, and electrode thickness on various DSSC parameters.

Keywords: DSSC, solar cell, photovoltaic

I. INTRODUCTION

In the last two decades, the dye sensitized solar cell (DSSC) has received much attention [1-8]. DSSCs have certain advantages over conventional silicon and thin film photovoltaic devices, due to the simplicity of the manufacturing process and the cost-effectiveness of most of the cell materials, which makes this type of solar cells feasible for mass production.

Currently, DSSC can achieve 11.1% energy conversion efficiency [9]. Further improvement is highly relied on better understanding of the energy conversion mechanisms and precise modeling for design optimization. In general, a DSSC comprises a nanocrystalline titanium dioxide (TiO_2) or zinc oxide (ZnO) electrode modified with a dye deposited on a transparent conducting oxide (TCO). A counter electrode is another TCO coated with a platinum (Pt) thin layer. An electrolyte solution with a dissolved iodide ion/triiodide ion redox couple (I^-/I_3^-) is added between the electrodes.

Efficient electron injection from excited dye to TiO_2 (or ZnO) plays an important role in DSSC [10,11]. The flow of the injected electrons through the porous TiO_2 film to the TCO depends on the incident intensity and trapping–detrapping effect [12]. Subsequently, the electrons flow to the counter electrode via an external load. The oxidized dye molecules are regenerated by redox mediators (I^-/I_3^-). Finally, for a complete DSSC operation cycle, the oxidized redox mediators (I_3^-) are transported to the counter electrode where regeneration of redox mediators occurs [13]. Due to the very small nanoparticle size (about 20nm) together with the strong screening effect of electrolyte, there is no significant macroscopic electric field in most of the porous thin films. Therefore, both electrons and redox mediators are transported mainly by diffusion.

The photoinjection of electrons from excited dye to TiO_2 conduction band increases the electron density in the porous electrode thin film, resulting in shifting the quasi-Fermi level E_F closer to the conduction band edge E_c. Theoretical models assume that the difference between E_F of TiO_2 and the electrolyte redox potential E_{redox} be the induced photovoltage [14-16]. That is true for the open-circuit condition in which there is no current flow through the TiO_2/TCO interface and electrolyte/counter electrode interface. However, under maximum power conditions, additional potential differences across these two interfaces should be considered.

This article describes a method to calculate the internal parameters of DSSC (L, α, m, D, n_0, τ). This approach provides a tool for researchers to estimate theoretically the internal parameters instead of digging through literature for their experimental value. Also, the effect of voltage loss at the counter electrode/electrolyte interface on the total voltage and the behavior of the cell are theoretically investigated.

II. MODELING

Due to the wide spread in DSSC research, the scientific community is interested in experimentally and theoretically investigation of the photoelectrochemical behavior of nanostructured electrodes of DSSC. Södrgren et al. [14] has suggested a simple model which is basically based on two equations. The first one is a
continuity equation that describes the transport, recombination, and generation of electrons within the nanoporous film:

$$D \frac{\partial^2 n(x)}{\partial x^2} - \frac{n(x) - n_0}{\tau} + \Phi_0 \alpha \exp(-\alpha x) = \frac{\partial n}{\partial t}$$  \hspace{1cm} (1)

where $n(x)$ is the excess concentration of the photogenerated electrons at position $x$ within the film measured from the TiO$_2$/transparent conducting oxide (TCO) interface, $n_0$ is the concentration of electrons under equilibrium conditions in dark, $\tau$ is the conduction band free electrons life time, $D$ is the diffusion coefficient of electrons, $\Phi_0$ is the illumination intensity (incident photon flux, cm$^{-2}$ s$^{-1}$), and $\alpha$ is the light absorption coefficient of the porous film. Under a steady-state condition of an irradiated DSSC, Eq. (1) becomes

$$D \frac{\partial^2 n(x)}{\partial x^2} - \frac{n(x) - n_0}{\tau} + \Phi_0 \alpha \exp(-\alpha x) = 0.$$  \hspace{1cm} (2)

The possibility of trapping-detrapping of electrons is not included in Eq. (2) since it is only important under nonsteady-state conditions [17]. Under short-circuit conditions, electrons are easily extracted as photocurrent and none of the electrons are drawn directly to the counter electrode. Therefore, the two boundary conditions are:

$$n(0) = n_0,$$  \hspace{1cm} (3)

and

$$\frac{dn}{dx}|_{x=d} = 0,$$  \hspace{1cm} (4)

where $d$ is the porous electrode thickness.

The second equation completing the model links the excess concentration of photogenerated electrons at the back contact, $n_{\text{contact}}$, with the photovoltage, $V_{ph}$, through the following expression [14, 18]

$$V_{ph} = \frac{kT}{q} m \ln \frac{n_{\text{contact}}}{n_0},$$  \hspace{1cm} (5)

where $k$ is the Boltzmann constant, $q$ is the elementary charge, $T$ is the absolute temperature and $m$ is an ideality factor. Equation (2) can be solved using the boundary conditions in Eq. (3), and Eq. (4). The short circuit current density $J_{sc}$ can be obtained as [14, 18]:

$$J_{sc} = \frac{q \Phi L \alpha}{1 - L^2 \alpha^2} \left[ -L \alpha + \tanh \left( \frac{d}{L} \right) + \frac{L \alpha \exp(-d \alpha)}{\cosh \left( \frac{d}{L} \right)} \right],$$  \hspace{1cm} (6)

where $L$ is the electron diffusion length given by:

$$L = \sqrt{D \tau}.$$  \hspace{1cm} (7)

If the DSSC operates under a potential difference $V$ between the Fermi level of the TiO$_2$ and the redox potential of the electrolyte, the density of the electrons at the TiO$_2$/TCO interface ($x = 0$) increases to $n$ giving a new boundary condition:

$$n(0) = n.$$  \hspace{1cm} (8)

The second boundary condition at $x = d$ remains unchanged as shown in Eq. (4). Solving Eq. (2) and using Eq. (5) yields the relationship between the current density and $V$ [14, 18]:

$$V = \frac{kT}{q} \ln \left[ \frac{L(J_{sc} - J)}{q D n_0 \tanh \left( \frac{d}{L} \right)} + 1 \right].$$  \hspace{1cm} (9)

This equation can be re-arranged to have the form:

$$J = J_{sc} - \frac{q D n_0}{L} \tanh \left( \frac{d}{L} \right) \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right].$$  \hspace{1cm} (10)

### III. Calculating the Internal Parameters of DSSC

To determine the internal parameters of DSSC ($\Phi$, $L$, $\alpha$, $m$, $D$), one needs five pieces of information. These pieces of information are the short circuit current ($J_{sc}$) given by Eq. (6), open circuit voltage ($V_{oc}$), current and voltage at the maximum power point ($J_{mp}$ and $V_{mp}$), respectively. The fourth and the fifth pieces of information required for the calculation of the five parameters can be obtained by realizing that the slope of the power at the maximum power point ($dP/dV_{mp}$) and ($dP/dJ_{mp}$) are equal to zero. Thus, at the open circuit voltage and at the maximum power point Eq. (9) becomes:

$$V_{oc} = \frac{kT}{q} \ln \left[ \frac{L J_{sc}}{q D n_0 \tanh \left( \frac{d}{L} \right)} + 1 \right].$$  \hspace{1cm} (11)

$$V_{mp} = \frac{kT}{q} \ln \left[ \frac{L (J_{sc} - J_{mp})}{q D n_0 \tanh \left( \frac{d}{L} \right)} + 1 \right].$$  \hspace{1cm} (12)

Additional two equations can be derived using the fact that on the P-V and P-J characteristics of a DSSC at the maximum power point, the derivatives of power with respect to voltage and with respect to current are equal to zero, that is:

$$\left( \frac{dP}{dV} \right)_{V = V_{mp}} = \frac{d(JV)}{dV} = J + \frac{dJ}{dV} V = 0.$$  \hspace{1cm} (13)

$$J = J_{mp}$$
The five internal parameters of DSSC \( (L, \alpha, m, D, n_0) \) can be obtained by simultaneously solving Eq. (6), and Eq. (11) through Eq. (14) using the Mathcad solve block (Given … Find) and by implementing the method of Conjugate Gradients. The value of the conduction band free electrons life time \( \tau \) is obtained by substituting the values of the electron diffusion length \( L \) and the diffusion coefficient of electrons \( D \) into Eq. (7), then, the J-V characteristics can be generated using Eq. (6) and Eq. (9). Calculations were done using light intensity \( \Phi = 1.0 \times 10^17 \text{ cm}^{-2} \text{s}^{-1} \) which is equivalent to 1 sun condition (100 mW/cm\(^2\)) [15,18,19], temperature \( T = 300 \text{ K} \), and porous layer thickness \( d = 10 \times 10^{-4} \text{ cm} \).

The values of \( J_{sc}, V_{oc}, J_{mp}, \) and \( V_{mp} \) are determined from the J-V characteristics obtained by substituting the published values of the parameters into Eq. (10) (see table I). Then, the obtained values of \( J_{sc}, V_{oc}, J_{mp}, \) and \( V_{mp} \) are implemented into Eq. (6), and Eq.(11) through Eq. (14) to obtain the internal parameters of the DSSC, see Table I. Notice that the calculated values are of the same order as the published values.

**TABLE I:** A comparison between the calculated values and the published values of DSSC internal parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Published value</th>
<th>Calculated value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L ) (cm(^{-1})s(^{-1}))</td>
<td>2.2361x10(^{-7})</td>
<td>2.0747x10(^{-3})</td>
</tr>
<tr>
<td>( \alpha ) (cm(^{-1}))</td>
<td>5000 Refs. [15,18,19]</td>
<td>5138.9831</td>
</tr>
<tr>
<td>( M )</td>
<td>4.5 Refs. [15,18,19]</td>
<td>4.4662</td>
</tr>
<tr>
<td>( D ) (cm(^{2})s(^{-1}))</td>
<td>5.0x10(^{-4}) Ref [18]</td>
<td>3.9353x10(^{-4})</td>
</tr>
<tr>
<td>( n_0 )</td>
<td>10(^{16}) Refs[ 18,20,21]</td>
<td>1.2911x10(^{16})</td>
</tr>
<tr>
<td>( \tau ) ms</td>
<td>10 Refs. [15,18,22]</td>
<td>10.9378</td>
</tr>
</tbody>
</table>

A good match between the current-voltage and the power-voltage characteristics obtained using the published values of the parameters [18], and the theoretically fitted current density-voltage and power-voltage curves obtained using the present method is illustrated in Fig. 1 and Fig. 2, respectively.

**IV. INTEGRATING THE MODEL**

Figure 3 illustrates the band energy levels of DSSC. In the dark, the potentials of TiO\(_2\), TCO, and the counter electrode are equal to the redox potential of the electrolyte as illustrated in Fig.3.a. Upon irradiation of the DSSC, the quasi-Fermi levels of TiO\(_2\) are raised due to photoinjection as illustrated in Fig.3.b. Therefore the reference photovoltage can be expressed as:

\[
V = V_0 - V_1 - V_2,
\]

where \( V_0 \) is the potential difference between the TiO\(_2\) Fermi level \( (E_F) \) and the redox potential of the electrolyte \( (E_{redox}) \). Here, \( V_0 \) represents the same voltage given in Eq. (9) and (10). On the other hand, \( V_1 \) is the voltage loss at
the TiO$_2$/TCO interface, and $V_2$ is the voltage loss at the counter electrode/electrolyte interface.

Fig. 3: Potential diagrams of DSSC: (a) in dark and (b) under illumination.

Meng et al [23] have suggested that highly doped and highly conductive TCO can be considered as a metal, and the TiO$_2$/TCO interface can be simulated by Schottky barrier model. Under illumination, the flow of electrons through the TiO$_2$/TCO interface causes a voltage loss $V_i$. This voltage loss can be correlated by the following expression referring to the thermionic emission theory:

$$J = A^* T^2 \exp \left( -\frac{q\phi_b}{kT} \right) \left[ \exp \left( \frac{qV_1}{kT} \right) - 1 \right],$$  \hspace{1cm} (16)

and

$$A^* = \frac{4\pi m^* qk^2}{h^3},$$  \hspace{1cm} (17)

where $\phi_b$ is Schottky barrier height; $h$ is Planck’s constant equal to 6.626x10$^{-34}$ m$^2$ kg s$^{-1}$, $m^*$ is equal to 5.6 times the free electron mass $m_e$ for TiO$_2$, and $A^*$ is Richardson’s constant of TiO$_2$ equal to 6.71 x 10$^6$ Am$^{-2}$ K$^{-2}$. Equation (16) can be rearranged to have the form:

$$V_1 = \frac{kT}{q} \ln \left[ 1 + \frac{J}{A^* T^2 \exp(-q\phi_b/kT)} \right]. \hspace{1cm} (18)$$

In order to find an expression for $V_2$, one needs to the following assumption that the charge transfer at the counter electrode is potential controlled, thus the current over the interface is independent of the concentrations of the redox ions at the interface. It is only dependent on the potential. Thus, the current can be described by the Butler-Volmer equation:

$$J = J_0 \left( \exp \left( \beta \frac{q}{kT} V_2 \right) - \exp \left( - (1 - \beta) \frac{q}{kT} V_2 \right) \right) \hspace{1cm} (19)$$

where $J_0$ is the exchange current density and $\beta$ is a symmetry parameter with a value ranges between 0 and 1. A symmetry parameter of 0.5 describes a charge transfer reaction, which is symmetric forward and reverse potential. In this article we assume symmetric reaction $\beta = 0.5$.

Expanding the two exponentials in Eq.(19), taking into account, only, the first three terms of the expansion of each exponential and simplifying terms yields:

$$J = J_0 \frac{q}{kT} V_2, \hspace{1cm} (20)$$

or,

$$V_2 = \frac{kT}{J_0 q} J. \hspace{1cm} (21)$$

A charge transfer resistance $R_{CT}$ of dimension $\Omega$ cm$^2$ thus can be defined as shown in Eq. (22). The dimension of $R_{CT}$ is the same as for a contact resistance.

$$\frac{1}{R_{CT}} = \frac{J_0 \frac{q}{kT}}{J}. \hspace{1cm} (22)$$
The charge transfer resistance is not too high, it is a good approximation to describe electrolyte/platinized TCO contact by an ohmic charge transfer resistance and the Nernest equation [21]. A low \( R_{CT} \) corresponds to a high exchange current density, which is essential for a DSSC with good performance [21]. The variation of \( R_{CT} \) with temperature is illustrated in Fig. 4. The exchange resistance increases with increasing temperature.

The diffusion controlled charge transfer reaction is not considered in this article since it is effective at higher voltage. In contrast, a Butler Volmerian behavior is observed at low voltages.

Meng et al. [23] showed that at the TiO\(_2\)/TCO interface there exists a critical value of \( \phi_b \), below which \( V_1 \) is negligible. At \( \phi_b \) value higher than the critical value, \( V_1 \) increases with increasing \( \phi_b \). In this article, a value of \( \phi_b \) equal to 0.5 eV which is below the critical value is chosen, in order to focus on the contribution of \( V_2 \) on the overall cell behavior.

Figure 5 illustrates a comparison between the calculated J-V characteristics using Eq. (9), \( V_0 \), and the effect of including the voltage loss at the TiO\(_2\)/TCO interface \( V_1 \); and the voltage loss \( V_2 \) at the counter electrode at 300 K. It is clear that inclusion of \( V_1 \) term doesn’t affect the J-V characteristics. On the other hand, the inclusion of the \( V_2 \) term affects the maximum power point location, but it doesn’t affect the short circuit current and the open circuit voltage points. The same behavior is found at higher temperature values. At lower temperature values, the inclusion of the voltage loss \( V_1 \) shows some deviation by lowering the maximum power point as shown in Fig 6.
higher series resistance contributes to the decrease in $V_{oc}$ and $V_{mp}$ [18].

The short circuit current and the maximum power current increase abruptly with increasing thickness as depicted in Fig. 8, then reach a peak, and decrease gradually afterward. The variations of $J_{sc}$ and $J_{mp}$ with thickness can be easily explained by electron photogeneration. For a given porosity and pore size, any increase in electrode thickness is directly increases the internal surface area of the semiconductor, resulting in a higher dye loading. Therefore, a thicker electrode can absorb more photons, leading to higher $J_{sc}$ and higher $J_{mp}$. However, if the thickness of the electrode is greater than the penetration depth, the number of photons useful for photogeneration of electrons will reach a limit causing no further increase in $J_{sc}$ and $J_{mp}$. Instead, an increase in the thickness beyond the light penetration depth yields more recombination centers that cause more electron loss and resulting in a gradual decrease in $J_{sc}$ and $J_{mp}$.

The J-V characteristics at various temperature values are depicted in Fig. 7. The open circuit voltage $V_{oc}$ as well as the maximum power increase with increasing temperature, and the short circuit current $J_{sc}$ is not affected as expected.

Figure 8 illustrates the variations of $V_{oc}$, $J_{sc}$, $J_{mp}$, and $V_{mp}$ with porous film thickness. The results show that $V_{oc}$ and $V_{mp}$ decrease monotonically with increasing film thickness. This phenomenon can be explained by the electron dilution effect [15]. As light is transmitted through the porous electrode, the intensity gradually decreases. Therefore, as the thickness increases, the excessive electron density becomes lower resulting in a decrease in $V_{oc}$ and $V_{mp}$. Also, a thicker electrode with a

![Graph of J-V characteristics at various temperatures.](image)

**Fig. 7:** The calculated J-V characteristics at various temperatures.

![Graph of $V_{oc}$, $J_{sc}$, and $V_{mp}$ vs. thickness.](image)

**Fig. 8:** The variations of $V_{oc}$, $J_{sc}$, $J_{mp}$, and $V_{mp}$ with porous film thickness.

![Graph of fill factor, efficiency, and maximum power vs. thickness.](image)

**Fig. 9:** The variations of fill factor, efficiency, and maximum power with electrode thickness.

The variations of fill factor, efficiency, and maximum power with electrode thickness is depicted in Fig. 9. The fill factor decreases with increasing electrode thickness, indicating an increase in the cell internal resistance. It is clear from the figure that the efficiency and the maximum power relation with thickness follow the same variation since the energy conversion efficiency of DSSC is the ratio of maximum output power to the incident light power. An optimal electrode thickness of
about 5 μm is inferred from Fig. 9 which is consistent with the theoretical finding of Ming. et al [18].

V. COMPARISON WITH PUBLISHED EXPERIMENTAL DATA

![Fig. 10: Comparison between the calculated data and published experimental data](image)

Fig. 10: Comparison between the calculated data and published experimental data from ref. [24] of V_{oc} vs. electrode thickness for Φ= 1.0x10^{17}cm^{-2}s^{-1}, α=5000 cm^{-1}, D=5.0x10^{-4}cm^{2}s^{-1}, m=4.5, and τ=10ms.

Although much work on DSSC has been published in literature, studies of the effect of electrode thickness are limited. In this section some relevant previous experimental work are presented for comparison with the modeling results of this investigation. Mercurochrome sensitized solar cells have been studied by Hara et al. [24] who investigated the effect of different photoelectrode materials, i.e. TiO_{2}, Nb_{2}O_{5}, ZnO, SnO_{2}, and In_{2}O_{3}. They found that as the thickness of TiO_{2} increased from 4.5 to 28 μm, the V_{oc} decreased from 0.58 to 0.48 V. The predicted V_{oc} by the current investigation agreed well with Hara et al. experimental data as shown in Fig. 10.

![Fig. 11: Comparison between the calculated data and published experimental data](image)

Fig. 11: Comparison between the calculated data and published experimental data from ref. [25] of J_{sc} vs. electrode thickness for Φ= 1.0x10^{17}cm^{-2}s^{-1}, α=5000 cm^{-1}, D=5.0x10^{-4}cm^{2}s^{-1}, m=4.5, and τ=10ms.

Fukai et al [25] have experimentally investigated the variation of J_{sc} with photoelectrode thickness using SnO_{2} as photoelectrode and using N719 dye as photon absorber. Figure 11 shows that the present modeling is consistent with the experimental work of Fukai et al [25] which shows that the measured J_{sc} increases significantly with electrode thickness and reaches the maximum at an electrode thickness of about 11 μm. Further increase in photoelectrode thickness would cause a slight decrease in J_{sc}.

The different values of optimal electrode thickness found by individual research groups may be attributed to different dye molecules of various light absorption coefficients. The microstructure parameters, such as TiO_{2} particle size, pore size, porosity, and roughness factor, have significant effects on the electron diffusion coefficient, electron life time, light absorption coefficient, as well as specific surface area, resulting in apparent difference in the DSSC performance [26-29]. Thus it is important to model the performance of a DSSC with respect to the microstructure of its photoelectrode [26,29].

VI. CONCLUSIONS

An accurate approach to calculate the internal parameters of a DSSC (L, α, m, D, n_{0}, τ) is proposed in this article. This method provides a tool for researchers to estimate theoretically the internal parameters instead of digging through literature for their experimental value. This approach is based on the electron diffusion differential model and the values of the short circuit current density J_{sc}, open circuit voltage V_{oc}, and the
current density and voltage at the maximum power point \( i.e. J_{mp} \) and \( V_{mp} \), respectively. By assuming that the charge transfer at the counter electrode is potential controlled, the Butler-Volmer equation is integrated with the electron diffusion differential model, and the Schottky barrier model to account for the interfacial effect at counter electrode/electrolyte and TiO\(_2\)/TCO interfaces on the J-V characteristics. Parametric analyses were conducted to study the effect of temperature, and electrode thickness on various cell parameters.

References