Electron Diffusion Model Based on I-V Data Fitting as the Calculation Method for DSSC Internal Parameters

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Abstract. Dye-sensitized solar cells (DSSC) made of TiO2 have received considerable attention from many researchers for the last three decades. Rapid theoretical and experimental studies have been conducted to improve the performance of DSSC. To understand the DSSC internal parameters, we need to fine-tune each component and identify the suitable conditions in optimizing the performance of assembled devices. In this work, we analyzed and calculated of several parameters the DSSC photoanode, e.g. electron diffusion and photon absorption coefficients. The experimental I-V data from solar simulator measurements were fitted base on electron diffusion model using Microcal Origin software. We compared the photon absorption coefficient values from this calculation method with the result of UV-Vis measurement and compared the electron diffusion coefficient values with the result of the SEM image data fitting calculation method. It was apparent that the results of I-V data fitting calculation method were comparable with the results of two other techniques.

Keywords: DSSC, diffusion model, I-V data fitting, electron diffusion coefficient, photon absorption coefficient

1. Introduction
One type solar cell of dye-sensitized (DSSC) combined of typical titanium dioxide (TiO2) is one of the most significant attention from many researchers for the recent decades after the work of O'Regan and Gratzel published in 1991 [1]. The DSSC is well known as a green and inexpensive photovoltaic device due to its natural available abundant materials and simple fabrication compared to two other type of solar cells [2]. From the milestone finding, extensive studies were expanded on the theoretical as well as experimental to improve the efficiency from 7.1% to 13% from 1991 to 2014. The latter is a criterion for the commercial application [3]. The current experimental studies on DSSC, such as [4–6], was a focus on material manufacture.
Theoretical modeling of the previous works [7–9] may provide better informed of how the system works. One of the theoretical modelings is the macroscopic diffusion model. The diffusion model had been developed to find an explicit equation of photocurrent as a function of thickness, light absorption, and light intensity by simplifying the actual DSSC mechanisms. In this model, the critical properties, cell design parameters, and operational parameters remain under consideration. This model was developed by Ferber [10] and then had been adopted by many researchers [11–15]. Recently, [16] had calculated DSSC electrical operational parameters such as the shunt resistance using Shockley’s equation fit analyses on $I$-$V$ data plot. This method performed good results in calculating DSSC electrical operational parameters, but this method could not estimate well the material properties and cell design parameters of DSSC. It is essential to obtain the internal parameters to search the fittest of each component and to identify the ideal conditions device performance. We report the calculation of material features and cell design parameters of DSSC such as diffusion coefficient using the macroscopic diffusion model based fit analyses on $I$-$V$ data.

2. Device Modelling

A stand-alone DSSC is generally consisted of a metal oxide semiconductor thin film supported by a suitable dye for the light absorbing charge transfer to form a photo-anode. This photo-anode is filled using specific electrolyte, e.g. iodide/tri-iodide redox and subsequently sandwiched onto two transparent conductive oxides (TCO) coated glass. The TCO coated glass faced to the prepared materials which were firstly covered with Pt or carbon as the catalyst of the redox reaction. The design of this device is depicted in Figure 1.

Figure 1. An illustrated Diagram of DSSC.

Figure 2 shows the working principle of DSSC. The photon is absorbed by the dye (1), and pump the electron to be excited (2). The injection of excited electron from the dye to the oxidic layer, (3) and then diffuse the TCO (4). From TCO, electron continues transferred to an external load to reach the counter electrode (5), through the $I/I^3$ electrolyte (6). To complete the cycle, the electron is then used by the electrolyte to regenerates the dye (7).
Figure 2. Working principle of DSSC

The processes above is called forward reaction which is the ideal cyclic of DSSC. However, there are some backward processes which reduce the efficiency of DSSC. The molecule of excited dye could oscillate to its ground state (a). This process can be neglected compared to the electron injection process (3) since the ratio of the relevant rate constants $k_3/k_a$ is about 1000 [F7]. The electron in the conduction band of oxide semiconductor could be caught by the non-ground state of dye-molecules (b), but since the rate constant $k_6$ is 100 times higher than $k_b$ (due to high iodide concentration), then this process is also can be neglected [F8]. Another possible process could happen as conducting band electron may be assigned by the tri-iodide electrolyte. This recombination process is necessary to be considered to enhance efficiency.

3. Theoretical Analysis

The total charge carriers current density in the cell are

$$j = eD_e \frac{\partial n_i}{\partial x} + en_e \mu_i E$$

where $e$, $E$, $D_e$, $\mu_i$, and $n_i$ is the electron charge, electrical field, charge carriers (electron, iodide, and tri-iodide ions) diffusion coefficient, mobility and density respectively. The first term represents the diffusion current and the second term is the drift current. In this approach, the drift current was neglected compared to the diffusion current.

The recombination rate of the electrons conduction band $R_e$ to the tri-iodide species could be obtained from first order kinetic arguments. By introducing a mean electron lifetime $\tau_e$ and by assuming of the recombination rate ($R_e$) is proportional to the difference of electron density $n_e$ from its equilibrium (dark).

$$R_e = \frac{n_e - \bar{n_e}}{\tau_e}$$

For other charge carriers is

$$R_i = \frac{n_i - \bar{n_i}}{\tau_i}$$

The photon flux is assumed given by

$$\phi(\lambda, x) = \phi(\lambda)e^{-\sigma(\lambda)x}$$

so, the incident photon rate is
\[- \frac{\partial \phi}{\partial x} = \alpha \phi e^{-\alpha x} \]  

(4)

and the electron generation rate is

\[ G(x) = \eta \int_{\lambda_0}^{\lambda_u} \alpha(\lambda) \phi_0(\lambda) e^{-\alpha(\lambda)x} \, d\lambda \]  

(5)

Where \( \alpha(\lambda) \), \( \lambda \), \( \phi(\lambda) \), and \( \eta \) are the absorption coefficient, wavelength, incident flux, and efficiency of electron injection, respectively. The integration limits reflect the characteristics of the absorptivity of the used of \( \beta \)-carotene. One photon is assumed to generate one electron as

\[ G_e(x) = \alpha \phi_0 e^{-\alpha(\lambda)x} \]  

(6)

The continuity of the number of charge carrier density is

\[ \frac{\partial j}{\partial x} + e \frac{\partial n}{\partial \tau} + eG_e(x) - eR_e(x) = 0 \]  

(7)

for steady-state equation, we have as

\[ \frac{\partial n}{\partial \tau} = 0 \]  

(8)

so, with neglecting the carrier drift currents, we have

\[ eD_e \frac{\partial^2 n}{\partial x^2} - e \frac{n - n_e}{\tau_e} + e\alpha \phi_0 \exp(-\alpha x) = 0 \]  

(9)

\[ \frac{\partial^2 n}{\partial x^2} - \frac{n - n_e}{L_i} + \frac{\phi_0 \alpha \tau_e e^{-\alpha x}}{L_i} = 0 \]  

(10)

with \( L_i \) is diffusion length defined as

\[ L_i = \sqrt{D_e \tau_e} \]  

(11)

Solving this differential equation for an electron in \( \text{TiO}_2 \) conduction band we get the electron density

\[ n_e(x) = n_0 + a \cosh \left( \frac{x}{L_e} \right) + b \sinh \left( \frac{x}{L_e} \right) + \frac{\alpha \phi_0 \tau_e}{1 - \alpha^2 L_e^2} \exp(-\alpha x) \]  

(12)

Then the current density is

\[ j_e(x) = eD_e \frac{\partial n_e}{\partial x} \]  

(13)

\[ j_e(x) = eD_e \left( a \sinh \left( \frac{x}{L_e} \right) + b \cosh \left( \frac{x}{L_e} \right) - \frac{\alpha \phi_0 \tau_e}{1 - \alpha^2 L_e^2} \exp(-\alpha x) \right) \]  

(14)

The \( a \) and \( b \) constants can be evaluated using these following boundary conditions

\[ n_e(0) = n_e \exp \left( \frac{eV}{mkT} \right) \]  

(15)

\[ \left. \frac{\partial n_e}{\partial x} \right|_{x=d} = 0 \]  

(16)
where \( V, k, T, m \) and \( n_0 \) is the bias voltage on the cell, Boltzmann constant, cell temperature, cell ideality factor and electron density in equilibrium (dark) condition.

\[
a = n_0 \left( \exp \frac{eV}{mkT} - 1 \right) - \frac{\alpha \phi \tau_e}{1 - \alpha^2 L_e^2}
\]

\[
b = \frac{\alpha^2 \phi_0 \tau_e L_e}{1 - \alpha^2 L_e^2} \alpha L e^{-ad} \frac{d}{L_e} - \frac{x}{L_e} \left( n_0 \left( \exp \frac{eV}{mkT} - 1 \right) - \frac{\alpha \phi_0 \tau_e}{1 - \alpha^2 L_e^2} \right)
\]

From Equation (14) and employing several conditions, the total electron current density equals the current density through the semiconductor, and TCO boundary (at \( x = 0 \)) can be written as

\[
\begin{align*}
\begin{array}{c}
j_{\text{total}} = \frac{e \phi L_e \alpha}{(1 - L_e^2 \alpha^2)} \\
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
j_{\text{total}} = \frac{e \phi D_e \tau_e \alpha}{(1 - D_e \tau_e \alpha^2)} \\
\end{array}
\end{align*}
\]

Which is similar to Shockley’s equation

\[
 j = j_{\text{sc}} - j_0 \left( \exp \frac{eV}{mkT} - 1 \right)
\]

The experimental result showed that the TiO\(_2\) porosity affects the light absorption and the electron diffusion coefficients [13]. The relation of porosity (\( P \)) and light absorption (\( \alpha \)) coefficient may be expressed as follow

\[
\alpha = 2568(1 - P)(P + 2.89)
\]

While the electron diffusion coefficients and the porosity is associated with

\[
D = a |P - P_c|^\mu
\]

where \( P_c, a, \) and \( \mu \) values fall to 0.76, 4 x 10\(^{-4}\) cm\(^2\) s\(^{-1}\), and 0.82, respectively [17].

4. Parametric Calculation

The parameters of DSSC such as the electron density in equilibrium or dark condition, ideality factor, electron lifetime, diffusion, and absorption coefficient were calculated by the I-V data fitting method using Microcal Origin software. The TiO\(_2\)-\( \beta \)-Carotene DSSC experimental I-V data plot was fitted using equation (19 b). The published experimental I-V data (we use the result of [18]) were digitized using GetData Graph Digitize 2.26 software and then fitted using equation (19 b). The useful initial parameters value input were listed in Table 1. The parameter's value after fitting process was listed in Table 2. The I-V curve and the fitting results of Fukai \textit{et al.} and the TiO\(_2\)-\( \beta \)-Carotene DSSC are shown in Figure 3 and Figure 4.
Table 1. The input parameters of model calculation

| Symbol | Description | Value | Ref. |
|--------|-------------|-------|------|
| $e$    | the electron charge | $1.60218 \times 10^{-19} \text{C}$ | - |
| $\phi_o(\lambda)$ | the incident photon flux | $1.0 \times 10^{17} \text{cm}^{-2} \text{s}^{-1}$ | [19] |
| $d$    | the thickness | $6 \times 10^{-4} \text{cm}$ | [18] |
| $D_e$  | the electron diffusion coeff. | $1.10 \times 10^{-4} \text{cm}^2 \text{s}^{-1}$ | [19] |
| $\tau_e$ | the electron lifetime | $10^{-2} \text{s}$ | [20] |
| $\alpha$ | the absorption coeff. | $5000 \text{cm}^{-1}$ | [21] |
| $n_o$  | the electron density in an equilibrium | $10^{11} \text{cm}^{-3}$ | [19] |
| $m$    | the ideality factor | 4.5 | [21] |

Table 2. The parameters extracted from the fitting result

| Symbol | Parameter value | Description |
|--------|-----------------|-------------|
| $e$    | $1.60218 \times 10^{-19} \text{C}$ | Constant |
| $\phi_o(\lambda)$ | $1.0 \times 10^{16} \text{cm}^2 \text{s}^{-1}$ | Constant |
| $d$    | $6 \times 10^{-4} \text{cm}$ | Constant |
| $D_e$  | $1 \times 10^{-4} \text{cm}^2 \text{s}^{-1}$ | Fitted. |
| $\tau_e$ | 0.00867 s | Fitted |
| $\alpha$ | 2127.74 cm$^{-1}$ | Fitted |
| $n_o$  | $1.0437122 \times 10^{11} \text{cm}^{-3}$ | Fitted |
| $m$    | 2.31826 | Fitted |

Figure 3. The fitting using Equation 19b on [18] $I-V$ data of TiO$_2$
Figure 4. The fitting properties using Equation 19b on TiO$_2$-β-Carotene I-V.

5. Comparison with Published Experimental Data

The diffusion and absorption coefficient obtained by the fitting method calculation were compared with the results of the calculation of equation (21) and (22). The [18] sample porosity was explicitly showed at their paper. The porosity of TiO$_2$-β-Carotene DSSC was calculated from the TiO$_2$-β-Carotene SEM image which showed in Figure 5 using Microcal Origin based 2D surface integral method. The 3D mapping of Figure 5 and the 2D surface integral result was shown in Figure 6. From Figure 6 we know that cell total volume of the sample was

$$V_{tot} = 5.4 \times 10^6$$

and the solid volume of 2D surface integral reached to 246651.006875. Based equation 24, we found that the porosity falls to 0.543212777.

$$P = \frac{V_{tot} - V_{solid}}{V_{tot}}$$

These values of porosity were then used to calculate the diffusion and absorption coefficient base on Equation 21 and 22. These obtained of diffusion and absorption coefficients are shown in Table 3.

| Porosity value obtained by calculation | Absorption coefficient (α) (cm$^{-1}$) | Diffusion coefficient (D) (cm$^2$ s$^{-1}$) |
|---------------------------------------|----------------------------------------|--------------------------------------------|
| Fukai et al. TiO$_2$-β-Carotene       | 3505.32                                 | 0.0000844                                  |
| Fukai et al. TiO$_2$-β-Carotene       | 4027.26                                 | 0.0001142 cm$^2$ s$^{-1}$                 |

Table 3. Diffusion and absorption coefficients calculated from the porosity
Based on Table 3 and 4, it was found that the difference of diffusion coefficient value obtained by $I$-$V$ data fitting method and by porosity based calculation was relatively small for both [18,22] and the TiO$_2$-$\beta$-Carotene sample. However, the difference of absorption coefficient value obtained by the $I$-$V$ data fitting method and by porosity based calculation was relatively large for both [18,22] and the TiO$_2$-$\beta$-Carotene sample. The percentage differences shown in Table 4 were calculated using Equation (26).
\[ R\% = \frac{X_{fs} - X_{por}}{X_{por}} \times 100\% \] (26)

**Table 4.** Percentage of diffusion and absorption coefficient calculation from the porosity

| Data Result            | R\% on Absorption coefficient (α) | R\% on Diffusion coefficient (D) |
|------------------------|-----------------------------------|----------------------------------|
| Fukai *et al.*         | 39.30                             | 18.48                            |
| TiO\textsubscript{2}-β-Carotene | 69.23                             | 12.43                            |

6. Conclusion

The diffusion and absorption coefficient obtained from DSSC *I*-\*V* data fitting has been compared with the porosity based on calculation. It was found that the diffusion coefficient obtained from the *I*-\*V* data fitting method and porosity based on calculation was acceptable for both [18,22] and the TiO\textsubscript{2}-β-Carotene sample. However, comparison of absorption coefficient value obtained by *I*-\*V* data fitting method and by porosity based on calculation was not acceptable for both [18,22] and the TiO\textsubscript{2}-β-Carotene sample.

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