An Optical and Electrical Modeling of Dye Sensitized Solar Cell: Influence of the Thickness of the Photoactive Layer

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Abstract Dye sensitized solar cells (DSSC) are used for photovoltaic applications. The paper presents a methodology for optical and electrical modeling of dye-sensitized solar cells (DSSCs). In order to take into account the scattering process, the optical model is based on the determination of the effective permittivity of the mixture and the scattering coefficient using Mie and Bruggeman theories, considering spherical particles. Then, from the radiative transfer equation, the optical generation rate of cell is deduced. Coupling the output of the optical model (the dye generation rate) to an electrical model for charge generation, transport, and first-order (linear) recombination, allows determination of current density and maximum power output. Due to our model, the dependence effects of the thickness of the photoactive layer upon the optical generation rate, the short circuit photocurrent density and the maximum power output are evidenced. Moreover, we see that when the thickness of the photoactive layer increases the optical generation rate increases. While, the short circuit current density and the maximum power output increase until d =10 µm then remain constant. Thereby, it was found that 10 µm of thickness is enough for the best I-V characteristics. Our results agree with those found in the literature.

Keywords: Dye sensitized solar cell, Bruggeman Theory, Mie Theory, Radiatives Transfers Equations, Mathematical Modeling, Matlab, Optical Generation Rate, Maximum Power Output, Thickness, Solar Cell


1. Introduction

Dye sensitized solar cells (DSCs) as alternative to solar cells have been widely studied in recent years [1,2,3]. Record efficiencies of over 11% have been achieved with ruthenium-complex sensitizers on laboratory-scale devices. [4,5,6] Dye sensitized solar cell is a mixture of nanostructured films, a sensitizer and an electrolyte containing the mediator sandwiched between two electrodes: a conductive oxide as an anode and a counter electrode as cathode as depicted in Figure 1. The efficiency of absorption of the incoming light by the dye is one of the paramount parameters for the cell performance. Accordingly, the peculiar composition of the photoactive layer makes the dye-sensitized solar cells very complicated to establish an optoelectronic model. Indeed, it is composed of a mixture of three materials (titanium dioxide, dye molecules and tri-iodide ions immersed within the electrolyte) which could raise homogeneity problems.

Various optical [7,8], electrical [9-18] and optoelectronic model [19,20] have been developed.

In this paper, a coupled optical and electrical model of dye-sensitized solar cell will be presented, putting a focus on the accurate description of the optics in the photoactive layer (by applying Bruggeman's theory, Mie's Theory and radiative transfer equations). The influence of the thickness of the photoactive layer is also studied.

The paper is organized as follows. In the next section, we introduce the coupled optical and electrical model. The comparison of the simulation with the literature is reported.
in the Results and Discussion section, which is followed by a Conclusions section.

2. Computational Model

The model considered is depicted in Figure 2. Thus, our study is essentially limited to the photoactive layer sandwiched between the two electrodes. The photoactive layer is a mixture of Titanium dioxide (TiO_2), a dye (Z907), a mediator and an electrolyte $I^- / I^+_3$.

2.1. Optical Model

By solving the equation of effective media (Equation 1), an analytical expression is obtained (equation 2, 3, 4):

$$X \frac{\varepsilon_a - \varepsilon_{Br}}{\varepsilon_a + 2\varepsilon_{Br}} + (1 - X) \frac{\varepsilon_b - \varepsilon_{Br}}{\varepsilon_b + 2\varepsilon_{Br}} = 0$$

$$n_{Br} = \sqrt{\frac{m(e_a, e_b, X)}{2}}$$

$$k_{ext, Br} = \frac{n(e_a, e_b, X)}{2n_{Br}}$$

$$\varepsilon_{Br} = n_{Br}^2 - k_{Br, ext}^2 + 2k_{Br, ext}n_{Br}$$

where $\varepsilon_a$ and $\varepsilon_b$ are the permittivity of the particles a and b, $\varepsilon_{Br}$ the effective permittivity and, X filling fraction of particle (a and b were TiO_2 or dye and/or mediator) following the case considered.

In order to apply the Bruggeman theory [21], as done by Rothenberger et al. [8], TiO_2 particles are supposed to be in a spherical shape, as well as the dye molecules, and the mixture electrolyte + mediator.

This previous theory is used in two different ways. One is a mixture of TiO_2 and dye and the other is a mixture of a [(nanostructured film+ dye) & (electrolyte+ mediator)].

The filling fraction of each individual component will be determined. For the mix of TiO_2 particle + dye the filling fraction of each individual component will be determined as follows:

We consider a diamond structure. Each TiO_2 particle admits four neighbors (coordination number CN = 4) [22,23]. The area occupied by the dye is given by the surface area of a sphere minus the reduction of surface area $CN\Delta S$. Meng et al [24] calculated the reduction of the surface area. His method will allow us to take into account the overlap distance $h$ in our calculation. In fact, $\Delta S$ is function of the overlap distance $h$, equal to $r_{TiO2}/100$, with $r_{TiO2}$ is the TiO_2 radius.

$$S_{colorant} = 4\pi r^2 - CN\Delta S$$

The number of dye is then deduced, assuming that each dye is a sphere of radius 1 nm. Thus, volumes (dye and TiO_2) are calculated and their filling fractions deducted. After determining the filling fractions, the effective permittivity of TiO_2-dye mixture is determined using equations (2), (3) and (4).

In the case of the mixture (TiO_2 +dye) / (electrolyte +mediator), the filling fraction of the electrolyte +mediator is equal to the porosity. Therefore, we determine the porosity.

We define the system as follows: First, the radius of all the nanoparticles are equal. Colloids considered perfectly spherical. The penetration length for two neighboring particles thus given by:

$$d_p = 2r(1 - h)$$

With $d_p$: distance between nanoparticles, $r$: radius of the sphere, $h$: the overlap distance.

Equation (5) can visualized in Figure 3.
h: overlap distance; CN: coordination number.

The first term on the right corresponds to the total volume of the sphere. The second term corresponds to the sum of the volumes of each spherical cap. Taylor et al. [25-26] used equations for the volume of single cell (6), the volume of sphere (7), and then obtained the following equation for the calculation of the porosity of a cell containing a number n of spheres

\[ P = 1 - \frac{n \pi}{\alpha_m} \left[ \frac{2 - CN \left( \frac{2h}{d} \right)^3}{12} + \frac{4 - CN \left( \frac{2h}{d} \right)^3}{8} \left( \frac{2h}{d} \right)^2 \frac{1}{12} + \frac{1}{6} \right] \]  

(8)

We will calculate the porosity for a diamond-like structure using equation (8) and Table 1. Thus, with the overlap distance h, equal to r_{TiO2}/100, we found P=0.64. The result of porosity agree with those found in literature. [19,22,23].

After determining the porosity, the filling fractions are deduced. Thus, the effective permittivity of the photoactive layer (TiO2-dye + electrolyte-mediator) is calculated using equations (2), (3) and (4).

\[ \gamma = \frac{\alpha_{abs} \times n_{abs}}{\alpha_{scat} \times n_{scat}} \]  

(9)

\[ S = \frac{\sigma_{scat} \times n_{scat}}{\sigma_{abs} \times n_{abs}} \]  

(10)

These results are inserted in the radiative transfer equation (4 flux) [29] to determine the expression of different flows. These expressions will be used for determining the absorption rate. The variation of these fluxes is gave by the following equations:

\[ \frac{dI_c(x)}{dx} = (K + S)I_c(x) \]  

(11)

\[ \frac{dI_d(x)}{dx} = -(K + S)J_c(x) \]  

(12)

where \( r_c, r_d, r_c^b, r_d^b \) the reflective coefficient of collimated beam, the reflective coefficient of radiation diffuse beam, the reflective coefficient of collimated beam at the back, the reflective coefficient of radiation diffuse beam at back side respectively.

\[ I_c^0 = \frac{1 - r_c^b}{1 - r_c} I_0 \]  

(17)

Here \( I_c^0 = 0; \) \( I_0 = \) incident light.

At the interface glass / mixed Zone

\[ I_c(a) = (1 - r_c) I_c^0 + r_c J_c(a) \]  

(15)

\[ I_d(a) = (1 - r_d) I_d^0 + r_d J_d(a) \]  

(16)

Thus, the local absorption rate per unit volume [8] established using the following expression:

\[ g(x) = KI_c(x) + KI_c(x) + \gamma KI_d(x) + \gamma JI_d(x) \]  

(20)

The optical photons absorption rate can then be deduced from g (x) [31]:

\[ G_d(x) = \frac{g(x)}{hc} \frac{\lambda}{\lambda} \]  

(21)

Finally, the optical photogeneration rate of the DSC given by:

\[ G(x) = G_d(x) \times \eta \]  

(22)

Where \( \eta \) is the injection rate.
2.2. Electrical Model

The charge generation function \( G_e(x) = \eta_{\text{dye}} G_{\text{dye}}(x) \), is coupled to an electrical model for free charge carriers. Here, for simplicity, we do not include ionic transport in the electrolyte and the reduction of triiodide at the counter-electrode. The electrical model is based on the stationary continuity equation. We suppose that there is no trapping states, i.e, the electron is only in the conduction band of the TiO\(_2\) layer. A purely diffusive transport equation for the electrical current density \( J \) is taken. \([9]\)

Then, in the ideal model case, only electrons from the conduction band can recombine with triiodide in the electrolyte, and the recombination rate is taken to be first order in \( n(x) \) (carriers density). This leads to an inhomogeneous linear differential equation for \( n(x) \)

\[
L^2 \frac{d^2 n(x)}{dx^2} - \left[ n(x) - n_0 \right] + \tau_0 G_e(x) = 0 \tag{23}
\]

Here, \( L = \sqrt{\frac{\tau_0 D_0}{\pi}} \) is the constant electron diffusion length, \( \tau \) is the electron lifetime, and \( n_0 \) is the electron number density at equilibrium in the dark. The electron number density in the dark \( n_0 \) is given by

\[
n_0 = N_c e^{\left( E_{F0} - E_c \right) / k_B T} \tag{24}
\]

where \( N_c \) is the effective density of the conduction band states, \( E_c \) is the conduction band energy, and \( E_{F0} \) is the Fermi level in the dark, which is equilibrated with the redox potential of the iodide/triiodide couple.

Based on both modeling and experimental results, effect of porosity \( P \) on the diffusion coefficient \( D_0 \) can be expressed as

\[
D_0 = a \left| P - P_c \right|^\mu \tag{32}
\]

where the constants \( a \) and \( \mu \), and the critical porosity \( P_c \) are 4.10\(^{-4}\) cm\(^2\) s\(^{-1}\), 0.82 and 0.76, respectively.

The boundary conditions to equation 23 are

\[
n(x = 0) = n_0 e^{\frac{V}{k_B T}} \tag{26}
\]

And

\[
\frac{dn}{dx} \bigg|_{x=d} = 0 \tag{27}
\]

where \( V \) is the photovoltage.

The general solution of (23) is given by

\[
n(x) = n_h(x) + n_p(x) \tag{28}
\]

Here

\[
n_h(x) = E e^{x/L} + F e^{-x/L} \tag{29}
\]

\[
n_p(x) = n_1(x) + n_2(x) + n_3(x) + n_4(x) \tag{30}
\]

\[
n_1(x) = I e^{ax}, \quad n_2(x) = J e^{-ax}, \quad n_3(x) = K e^{bx}, \quad n_4(x) = M e^{-bx} \tag{31}
\]

Where \( E \) and \( F \) are constants determined by the boundary conditions. \( I, J, K \) and \( M \) function of the generation rate.

From the complete solution for \( V = 0 \), the photocurrent density at short circuit can be calculated by

\[
J_{sc} = e D_0 \left. \frac{dn}{dx} \right|_{x=0} \tag{32}
\]

3. Results and Discussions

The analytical model presented above is validated with experimental data reported in the literature (Figure 4, Figure 5).

We make here (Figure 4) a comparison between our results and those of Wenger et al. \([19]\) Here we see that for the same radii (\( r = 20 \) nm); we have almost the same values, but with different paces. When we the radius is 40 nm the paces are almost the same. This can explained by the fact that Wenger et al extracted the coefficients experimentally and the radius are rarely homogeneous \([33]\) in that case, which may be the cause of our differences.

The analytical model presented above validated with experimental data reported in the literature. The modeling of solar cell performance in terms of short-circuit photocurrent is compared with the experimental measurements reported by Saito et al. \([34]\) (Figure 5). The normalized modeling and experimental results plotted in Figure 5 show a good agreement. These results show also a good agreement with other result in literature \([35]\).

Figure 4. the generation rate of the dye depending on the depth of the cell

Figure 5. Short circuit photocurrent density as a function of overlap distance

Figure 6 shows the generation rate as a function of the thickness of the photoactive layer \( d \). We see that when \( d \)
increases the generation rate increase. In fact, the TiO$_2$ particles increase and then the dye molecules.

Then, in Figure 8, we see that when d increases the maximum power output $P_{\text{max}}$ increases until $d=10 \ \mu$m but remains practically constant after 10 $\mu$m. Therefore, according to our model, a thickness of 10 $\mu$m is adequate for a good efficiency of dye-sensitized solar cell. This result agree well with those found on literature. [36,37] Indeed, Huang et al [37], show that for a good efficiency, a thickness of 12 $\mu$m of TiO$_2$ film is adequate.

4. Conclusion

Our model allows us to see the influence of the thickness of the photoactive layer $d$ on the generation rate, the short circuit current density $I_{sc}$, the open circuit voltage $V_{oc}$ and the maximum power output $P_{\text{max}}$.

Thus, we see that when the thickness of the photoactive layer $d$, the generation rate increases. However, $I_{sc}$ and $P_{\text{max}}$ increase until $d=10 \ \mu$m, then remain constant. While, $V_{oc}$ remains constant.

Then, according to our model, a thickness of 10 $\mu$m is enough for a dye-sensitized solar cell with good characteristics. Our results agree with the ones found in the literature.

However, this model has some limitation: the particles are not necessarily spherical and of the same size and the difference between the reflected coefficient diffused and collimated could be taken into account for better precision.

References

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