TOPICAL REVIEW

Review of diffusion models for charge-carrier densities in dye-sensitized solar cells

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Keywords: dye-sensitized solar cells, titanium dioxide, diffusion, Beer–Lambert, mathematical modelling

Abstract

Originated in 1991 by O’Regan and Grätzel, dye-sensitized solar cells (DSSCs) provide alternative solutions for renewable energy problems. Earlier mathematical models for DSSCs are based on junction solar cells, which was first studied by Chapin et al in 1954. These equations were derived from Shockley’s work on modelling semiconductors in the late 1940s. However, it was pointed out by Cao et al and Gregg that diffusion model is more suitable for modelling DSSCs. Since the study by Södergren in 1994, the diffusion model has become prevalent in literature and the development of this model by including additional equations to incorporate electrolyte concentrations, time dependence for charge carrier densities and nonlinear diffusivity has shown to capture more complex processes of charge transport within DSSCs. In this paper, we review the development of the diffusion model for the charge carrier densities in a conduction band of DSSCs.

1. Introduction

The demand for renewable energy is greater than ever, with Earth’s oil reserves expected to expire by the end of the century [1]. Though 85% of the world’s energy demands are met by fossil fuels [2], the renewable energy sector is projected to fulfill 33% of the world’s energy supplies by 2030 [3].

Since their inception in 1991, dye-sensitized solar cells (DSSCs) have proven a unique, low-cost approach to harvesting renewable energy [4]. Standard DSSCs comprise four fundamental components, namely photosensitive dye, nanoporous semiconductor, electrolyte couple and counter electrode. Figure 1 outlines the components of a DSSC together with their intended functionality (outlined in the following section). DSSCs offer flexibility in the selection of materials and the design of these components, creating an active niche of research.

1.1. Function of DSSCs

In essence, there are seven main chemical reactions used to describe DSSCs in operation [1, 6]. Four of these chemical reactions enhance the performance of DSSCs, whereas the other three mechanisms are detrimental to the generation of electricity.

In DSSCs, photosensitive dye molecules absorb photons and enter an excited energy state:

\[ S + h\nu \rightarrow S^* , \]

where \( S \) is the dye molecule, \( h \) is Planck’s constant and \( \nu \) is the frequency of the photon. The photosensitive dye is designed to use this excited energy state to donate (or inject) electrons into the semiconductor’s conduction band:

\[ S^* \rightarrow S^+ + e_{CB}^-. \]

The photosensitive dye is regenerated by the electrolyte couple:

\[ S^+ + M \rightarrow M_{ox} + S, \]

where \( M \) is the electrolyte and \( M_{ox} \) is the oxidized electrolyte. This process enables the chemical reaction (1) to repeat. Finally, regeneration of the electrolyte is carried out by the counter electrode:
As a result of chemical reactions (1) to (4), a DSSC is able to generate electricity provided that there is sufficient sunlight as an energy input. However, DSSCs are also subject to loss mechanisms, which generally involve recombination of electrons at interfaces. Excited dye molecules do not necessarily inject electrons into the conduction band as described by chemical reaction (1), instead they may emit the photon as radiation:

\[ \text{S}^* \rightarrow \text{S} + h\nu. \]  

(5)

Alternatively, injected electrons may recombine with the DSSC before leaving the device to power a load. Active electrons in the semiconductor’s conduction band may be used for regeneration either in the dye or in the electrolyte, which are respectively described by

\[ \text{S}^+ + e_{\text{CB}} \rightarrow \text{S}, \]  

(6)

\[ \text{M}_{\text{ox}} + e_{\text{CB}} \rightarrow \text{M}. \]  

(7)

Construction of DSSCs must therefore enhance reactions (1) to (4) and reduce the potential loss of electrons through the processes (5) to (7).

1.2. Components of DSSCs

1.2.1. Photosensitive dyes

The unique feature of DSSCs is its photosensitive dyes which are used to absorb sunlight [6]. Even though several types of dye molecules have already been proposed, the development of new dyes continues an active area of research.

One of the dyes that saw continual use since its introduction is the Ruthenium(II) N3 dye [7, 8]. The relationship between the molar absorption coefficient of N3 dye and the wavelength is given in figure 2 [8]. In their paper, Wu et al [8] show that the molar absorption coefficients of CYC-B1 and CYC-B5 dyes are generally higher than that of N3 dye, despite their inferior performances at lower wavelengths. However, the Ruthenium based N3 dye has continued its popularity, owing to its broad light absorption spectrum, increased duration in the excited state and high thermal stability [9, 10].

Another well-known Ruthenium based dye is N719 [3]. The absorption coefficient of N719 relative to the wavelength is shown in figure 3 [11]. From the figure, we see that the absorbance of the N719 dye is greatly improved when anchored to the ZnO semiconductor as opposed to TiO2.
1.2.2. Nanoporous semiconductor

Given that the nanoporous semiconductor is responsible for the bulk of the electron transport in DSSCs, the choice of semiconductor is extremely important. A nanoporous semiconductor requires a wide band gap, which allows electrons to easily receive energy from excited dye molecules. In table 1, we summarise commonly used semiconductors together with their band gaps and efficiencies [12].

From table 1 we see that TiO₂ vastly surpasses other semiconductors by way of efficiency. In their paper, Lau et al [12] show that TiO₂ is generally regarded as superior for its wide band gap, low cost and resistance to photocorrosion. Figure 4 shows the porous structure of TiO₂ under electron microscope [13].

### Table 1. Nanoporous semiconductors used in DSSCs [12].

| Semiconductor | Band Gap | Efficiency  |
|---------------|----------|-------------|
| TiO₂          | 3.23     | 12.30%      |
| ZnO           | 3.30     | 5.60%       |
| Nb₂O₅         | 3.49     | 5.00%       |
| Zn₂SnO₄       | 3.70     | 3.70%       |
| SrTiO₃        | 3.20     | 1.80%       |
| WO₃           | 2.60–3.00| 0.75%       |
| SnO₂          | 3.60     | 0.30%       |

Figure 2. Relationship between molar absorption coefficient and wavelength (nm) for three commonly used dyes (N3, CYC-B1 and CYC-B5). Reprinted from [8], Copyright (2010), with permission from Elsevier.

Figure 3. Plot of N719 absorbance against wavelength (nm). Reprinted from [11], Copyright (2019), with permission from Elsevier.
1.2.3. Electrolyte couple
The electrolyte couple (sometimes referred to as the redox couple or charge mediator [6]) in the DSSC is designed to regenerate the photosensitive dye once it has been ionized by the process of electron injection (via reactions (1) and (3)). The iodide-triiodide redox couple I\(^-\) - I\(_3\)\(^-\) is used almost universally [1, 14–18], since other electrolytes such as Br\(^-\) - Br\(_3\)\(^-\) and SCN\(^-\) - SCN\(_3\)\(^-\) exhibit poor power conversion efficiencies compared to iodide-triiodide redox couple [19].

1.2.4. Counter electrode
Within a functioning DSSC, the counter electrode reintroduces electrons back to the DSSCs by allowing the electrolyte to replace the electrons lost in dye regeneration (as shown in reaction (4)) [6]. Counter electrodes are typically platinum (as seen in [12, 14, 15, 17, 18, 20–25]). Although known for its efficiency, major deterrents for using platinum as a counter electrode include its scarcity (increasing production costs) [26] as well as its instability when it is used in conjunction with corrosive electrolyte couples [27].

In 2007, carbon nanomaterials were found to provide a unique and novel solution to both issues associated with the use of platinum counter electrodes [27–29]. In particular, Huang et al [28] investigate a DSSC with hard carbon spherule (HCS) as counter electrode. Though its efficiency of 5.7% is lower than the benchmark 6.5% of the DSSC with Platinum counter electrode, there are improvements in conductivity and resistance to corrosion.

1.3. Mathematical models
One approach to modelling DSSCs is based on the study of traditional junction solar cells. In particular, the drift-diffusion equations are used to describe the electron density in the semiconductor’s conduction band while the hole density in the semiconductor’s valence band and the strength of the electric field are modelled by Poisson’s equation [2, 15, 30]. These equations are inherited from the models for the silicon solar cells pioneered by Chapin et al [31] and are based on Shockley’s mathematical models for semiconductors [32]. Although this approach may benefit from the studies in the past decades, Gregg [33] mentions that it is not necessarily the best modelling approach for DSSCs. This is because the electric field is considered to have a negligible effect on the overall operation of DSSCs and is therefore ignored in subsequent models of DSSCs [22]. In this paper, we review the development of the diffusion models for DSSCs.

2. Diffusion model
The diffusion model is used to determine the electron density in the semiconductor’s conduction band of a DSSC. Based on the electron density, other important parameters related to the performance of DSSCs can be obtained, including the short-circuit current density \(J_{sc}\), the open-circuit voltage \(V_{oc}\) and eventually the efficiency \(\eta\).
2.1. Diffusion equations

Due to the structure of DSSCs, only one spatial dimension is considered. Given a DSSC of thickness \( d \), we orient the device so that the counter electrode is located at \( x = d \). From this, the conduction band electron density \( n(x, t) \) at position \( x \) and time \( t \) in the DSSC obeys the following partial differential equation (PDE) [34]:

\[
\frac{\partial n}{\partial t} = \frac{\partial}{\partial x} \left[ D(n) \frac{\partial n}{\partial x} \right] + G(x) + R(n),
\]

where \( D(n) \) is the density-dependent diffusion coefficient, \( G \) is the spatially dependent electron generation term and \( R(n) \) is the density-dependent recombination term. For DSSCs, we assume no electron flux at the counter electrode, giving rise to the boundary condition [35]

\[
\frac{\partial n}{\partial x} \bigg|_{x=d} = 0.
\]

The electron density at the TCO interface \((x = 0)\) is dependent on the bias voltage \( V \) on the DSSC [36], and is given by

\[
n(0, t) = n_{eq} e^{\frac{qV}{k_BT}},
\]

where \( n_{eq} \) is the dark equilibrium electron density, \( m \) is the ideality factor, \( q \) is the electron charge, \( k_B \) is Boltzmann’s constant and \( T \) is the temperature of the DSSC. For short-circuit conditions, we set \( V = 0 \) and use the resulting boundary condition \( n(0, t) = n_{eq} \). Under open-circuit conditions \((J = 0)\), an alternative boundary condition for \( x = 0 \) is given by [37]

\[
\frac{\partial n}{\partial x} \bigg|_{x=0} = 0,
\]

which allows us to compute the electron density if \( V_{oc} \) is unknown. The DSSC is assumed to be initially at equilibrium, giving the simple initial condition

\[
n(x, 0) = n_{eq} e^{\frac{qV}{k_BT}}.
\]

This model was developed in 1994 by Södergren et al [36], in which the steady-state special case was considered under the assumptions of linear diffusion and recombination with the boundary conditions based on short-circuit conditions \((V = 0)\). This diffusion model is a popular choice for modeling DSSCs (as seen in [20, 36–39]). In particular, the linear diffusion equation is coupled with electrolyte equations in some models (which are discussed in more detail in section 2.5).

In 1996, Cao et al [22] extended this model to include time dependence, resulting in the first PDE for electron diffusion. This paper also suggested the first nonlinear version of the equation, with the diffusion coefficient \( D(n) = n \).

2.2. Diffusion coefficient

The diffusion coefficient \( D(n) \) in equation (8) is an important component, as it reconciles the boundary condition \( n(0, t) = n_{eq} \) with the source term \( G(x) \) that is typically at its maximum at \( x = 0 \). In the diffusion model of Södergren et al [36], the diffusion coefficient is assumed to be a constant,

\[
D(n) = D_p.
\]

Though many papers adopt a constant value for \( D_p \) [35, 36, 40], a study in 2006 introduced a model incorporating the effect of the porosity of the nanoporous semiconductor into the diffusion coefficient [38].

In particular, Ni et al [38] gave the following expression for the diffusion coefficient that is dependent on the porosity \( p \) of the nanoporous semiconductor (\( TiO_2 \) in this case):

\[
D_p(p) = 1.69 \times 10^4 (-17.48p^3 + 7.39p^2 - 2.89p + 2.15).
\]

2.3. Electron generation models

The electron generation term \( G(x) \) in (8) is a source term designed to incorporate the increase of conduction band electrons induced by sunlight exposure. The Beer–Lambert model is used exclusively, and is given by

\[
G(x) = \int_{\lambda_{min}}^{\lambda_{max}} \eta_{ij} \phi(\lambda) \alpha(\lambda) e^{-\alpha(\lambda)\lambda} d\lambda,
\]

where photons absorbed are in the wavelength range \([\lambda_{min}, \lambda_{max}]\), \( \eta_{ij} \) is the electron injection efficiency (the proportion of electrons successfully injected into the semiconductor conduction band, also referred to as \( \Phi_{ij} \) and \( \eta_{ij} \)), \( \phi \) is the wavelength-dependent incident photon flux and \( \alpha \) is the wavelength-dependent absorption coefficient of the photosensitive dye.
For ease of computation, several papers omit wavelength dependence in (14) (such as [22, 37, 41, 42]), leading to a simplified Beer–Lambert model of the form

\[ G(x) = \eta_{\text{int}} \varphi \alpha e^{-\alpha x}, \tag{15} \]

where \( \varphi \) is an integrated version of \( \phi \) and wavelength dependence of \( \alpha \) is omitted. This generalized form of the Beer–Lambert law is also used in [43–45], for example.

We comment that equation (15) was first introduced by Södergren et al [36], who considered two simplified forms of (14). The first form, which is 15, assumes that substrate-electrode (SE) illumination is located at \( x = 0 \). The second form assumes that electrolyte-electrode (EE) illumination is located at \( x = d \). In this case, the Beer–Lambert law is of the form [20, 46]

\[ G_{EE}(x) = \varphi \alpha e^{\alpha(x-d)}. \tag{16} \]

Finally, an analytical approach to model the electron generation term was developed by der Maur et al [16]. Their analytical model is motivated by relaxing the assumption of a constant absorption coefficient in DSSC modelling. By applying a rate equation to the density of photoactive dye molecules and a continuity equation on the electron generation term, their model for electron generation term, referred to here as \( g(x) \), is given implicitly by

\[ g(x) e^{\tau_r \sigma(x-x_0)} = g(0) e^{-D_0 \alpha x}, \tag{17} \]

where \( \tau_r \) is the dye regeneration time, \( \sigma \) is the attenuation cross section of the absorbing dye molecule and \( D_0 \) is the total density of photoactive dye molecules. If \( \tau_r = 0 \), we recover the classical Beer–Lambert model \( g(x) = g(0) e^{-D_0 \alpha x} \). This extended model allows the DSSC modelling to incorporate the effect of light intensity on electron generation within an operating DSSC.

2.3.1. Incident photon flux

Central to the Beer–Lambert equation (14) is the incident photon flux \( \phi \), which is the input from sunlight. Figure 5 is a plot of \( \phi \), the measured AM1.5 solar spectrum against wavelength \( \lambda \) [47].

The literature models the input of sunlight in solar cells by two expressions, namely the incident photon flux and the sunlight intensity. Though equivalent, the incident photon flux considers the photons per unit area provided by sunlight, which has unit m\(^{-2}\)s\(^{-1}\). On the other hand, sunlight intensity is a measurement of the AM1.5 solar spectrum, which considers sunlight as energy per unit area, so that the unit is given by Wm\(^{-2}\). Dividing the sunlight intensity (Wm\(^{-2}\)) by energy (Joules), we can convert from the sunlight intensity to photon flux (m\(^{-2}\)s\(^{-1}\)). Here, the energy we use is defined as the energy of a photon,

\[ E = \frac{hc}{\lambda}, \]

where \( h \) is Planck’s constant, \( c \) is the speed of light and \( \lambda \) is the wavelength of the photon.
In the Beer–Lambert expression \( G(x) \), \( \phi \) is usually considered as a photon flux and assumed to be a constant \( \varphi \). The majority of the literature agrees upon \( \varphi = 10^{17} \text{ cm}^{-2} \text{s}^{-1} \) [37–39, 48, 49]. Nevertheless, other values used for \( \varphi \) include \( 1.5 \times 10^{17} \) [1], \( 4.5 \times 10^{15} \) [20], \( 9.87 \times 10^{16} \) [41], \( 5 \times 10^{16} \) [50] and \( 8.19 \times 10^{16} \text{ cm}^{-2} \text{s}^{-1} \) [51].

Instead of assuming \( \phi \) as a constant \( \varphi \), we can use Planck’s law, or an approximation to Planck’s law to prescribe \( \phi \) as a function of wavelength [52], namely

\[
\phi(\lambda) = \frac{2\pi \hbar c^2}{\lambda^3} [e^{\frac{\lambda}{kT}} - 1]^{-1}. \tag{18}
\]

Integrating \( \phi \) over all wavelengths, we have

\[
\varphi = \int_0^\infty \phi(\lambda)d\lambda = \int_0^\infty 2\pi \hbar c^2 \lambda^3 [e^{\frac{\lambda}{kT}} - 1]^{-1}d\lambda
\]

\[
= (2\pi^2\hbar^2)k_B T^4 \Gamma(4)\zeta(4),
\]

where \( \Gamma \) is the gamma function defined by \( \Gamma(z) = \int_0^\infty x^{z-1}e^{-x}dx \) and \( \zeta \) is the Riemann zeta function, given in its integral definition by [53]

\[
\zeta(s) = \frac{1}{\Gamma(s)} \int_0^\infty x^{s-1}e^{-x}dx.
\]

As \( \Gamma(4) = 3! = 6 \) and \( \zeta(4) = \pi^4/90 \) [54], we obtain

\[
\varphi = \frac{2\pi^3 k_B^4 T^4}{15c^2\hbar^3}. \tag{19}
\]

Under the standard temperature \( T = 5800 \text{ K} \), we have \( \varphi \approx 6.4168 \times 10^7 \text{ Wm}^{-2} \). This value justifies the assumption of a constant \( \varphi = 10^{17} \text{ cm}^{-2} \text{s}^{-1} \) as used in [37–39, 48, 49].

Alternatively, Anta et al [40] define the incident photon flux as

\[
\phi(\lambda) = \frac{2Fc}{\lambda^2} e^{-\frac{\lambda}{kT}}, \tag{20}
\]

where \( F \in [0, 1] \) is an irradiance coefficient used to measure the intensity of the sunlight. Integrating this form of \( \phi \) over all wavelengths gives

\[
\varphi = \int_0^\infty \phi(\lambda)d\lambda = \int_0^\infty \frac{2Fc}{\lambda^2} e^{-\frac{\lambda}{kT}}d\lambda
\]

\[
= \int_0^\infty 2Fc \left( \frac{k_B T}{\hbar c} \right)^4 x^4 e^{-x} \left( \frac{\hbar c}{k_B T} \right)^2 x^{-2}dx \ 	ext{ with } x = \frac{\hbar c}{k_B T}
\]

\[
= 2Fc \left( \frac{k_B T}{\hbar c} \right)^4 \int_0^\infty x^2 e^{-x}dx = 2F \left( \frac{k_B T}{\hbar c} \right)^3 \Gamma(3) = 4F \left( \frac{k_B T}{\hbar c} \right)^3. \tag{21}
\]

Using \( F = 1 \) and \( T = 5960 \text{ K} \) [40], we find \( \varphi \approx 8.5237475580 \times 10^{23} \text{ m}^{-2} \text{s}^{-1} \).

Finally, Malyukov et al [55] propose the integral equation for \( \phi \) as

\[
\varphi = \int_{\lambda_{min}}^{\lambda_{max}} C \left( \frac{R_s}{r_0} \right)^2 \left( \frac{2\pi FC}{\lambda^2} \right) [e^{\frac{\lambda}{kT}} - 1]^{-1}d\lambda, \tag{21}
\]

where \( C \) is a coefficient used to model the atmosphere’s influence on available photons for the DSSC, \( R_s \) is the radius of the Sun and \( r_0 \) is the average distance from Earth to the Sun. The parameter \( F \) has the same meaning as in the model by Anta et al [40]. Integrating this expression over all possible wavelengths, we find
The wavelength-dependent absorption coefficient $\alpha(\lambda)$ (sometimes referred to as $\alpha_{ab}$) to avoid ambiguity with other parameters with the same name) is usually assumed to be a constant, despite a clear relationship with wavelength as shown in figures 2 and 3.

Other model for $\alpha$ is given by Ni et al [38] where the absorption coefficient is assumed to be dependent on porosity $p$ of the nanoporous semiconductor, namely

$$\alpha(p) = 2.97 \times 10^4 p^2. \quad (22)$$

### 2.4. Recombination models

In contrast to the electron generation, electron recombination has seen a great variety of modelling approaches. The first such model is shown in Södergren et al [36] which is given by

$$R(n) = -\frac{n - n_{eq}}{\tau_0},$$

where $n_{eq}$ is the dark equilibrium density and $\tau_0$ is the electron lifetime. Referred to as the first order recombination [35, 36], this model is used frequently for its simplicity (used in [20, 37–39, 41, 46, 49, 55]).

Simple extension to this recombination term includes introducing nonlinear recombination rate (as considered in Fisher et al [58] and Barnes et al [48]):

$$R(n) = -k_R(n - n_{eq})^\beta,$$

where $k_R = 1/\tau_0$ is a recombination constant and $\beta$ is the order of recombination. In particular, Fisher et al [58] consider second order recombination ($\beta = 2$) and Barnes et al [48] consider $0 < \beta < 1$.  

| Value          | Author                        | References |
|----------------|-------------------------------|------------|
| $9.87 \times 10^{20}$ | Lee et al 2004                | [41]       |
| $10^{21}$       | Gómez and Salvador 2005       | [37]       |
| $8.52 \times 10^{23}$ | Anta et al 2006               | [40]       |
| $4.5 \times 10^{19}$ | Barnes et al 2009             | [20]       |
| $1.5 \times 10^{21}$ | Andrade et al 2011           | [1]        |
| $5 \times 10^{10}$    | Bertoluzzi and Ma 2013        | [50]       |
| $8.19 \times 10^{20}$ | Shi et al 2013                | [51]       |
| $4.81 \times 10^{11}$ | Malyukov et al 2014          | [55]       |

### Table 2. Numerical values for the constant $\varphi$ used in DSSC modelling (in m$^{-2}$s$^{-1}$).

$$\varphi = \int_0^\infty C \left( \frac{R_s}{r_0} \right)^2 \left( \frac{2\pi CF}{\lambda^2} \right) \left( e^{\frac{\lambda^\alpha}{kT}} - 1 \right)^{-1} d\lambda$$

$$= 2\pi CF \left( \frac{R_s}{r_0} \right)^2 \int_0^\infty \lambda^4 \left( e^{\frac{\lambda^\alpha}{kT}} - 1 \right)^{-1} d\lambda$$

$$= 2\pi CF \left( \frac{R_s}{r_0} \right)^2 \left( \frac{k_B T}{\hbar} \right)^3 \int_0^\infty x^2 (e^x - 1)^{-1} dx \quad \text{with} \quad x = \frac{\hbar c}{\lambda k_B T}$$

$$= 2\pi CF \left( \frac{R_s}{r_0} \right)^2 \left( \frac{k_B T}{\hbar} \right)^3 \Gamma(3) \zeta(3)$$

$$= 4\pi CF \left( \frac{R_s}{r_0} \right)^2 \left( \frac{k_B T}{\hbar} \right)^3 \zeta(3).$$

Though there is no analytical expression for $\zeta(3)$, the result is a finite number known as Apéry’s constant [36]. With $R_s = 6.9951 \times 10^4$ m [57], $r_0 = 1.495978707 \times 10^{11}$ m [57] and $F = 1$, we have $\varphi \approx 4.8144702590 \times 10^{14}$ m$^{-2}$s$^{-1}$.

The values of $\varphi$ from the literature and from the above derivations are summarised in table 2 (given in units m$^{-2}$s$^{-1}$).
A slight modification of this model is given in Anta et al.\[40\] as

\[ R(n) = -k_b \left( \frac{n}{n_{eq}} \right)^3 (n - n_{eq}). \]

This recombination term is used in [40] in conjunction with the diffusion coefficient \( D(n) = D_0 (n/n_{eq})^\beta \). The extra factor \((n - n_{eq})\) is introduced to facilitate the effectiveness of recombination based on the electron density and its relative distance from equilibrium.

Finally, in Nithyanandam et al.\[2\] and Tanaka\[59\], a nonlinear recombination model is proposed to incorporate the role of the electrolytes in the DSSCs:

\[ R_e(x) = -k \left( n_e(x) \right) \frac{n_{i_e}(x)}{n_{i}(x)} - \tau_e \sqrt{n_{i_e}(x) n_{i_e}}, \]

where the bar notation denotes the equilibrium values. This equation together with the model proposed by Nithyanandam et al.\[2\] are not popularly used for DSSCs. This is because the model is based on a drift-diffusion equation, and since the effect of drift is negligible in DSSCs[22,33], pure diffusion models are more widely adopted for DSSCs.

2.5. Electrolyte densities

The diffusion equation given by (8) is primarily concerned with the electron density in the conduction band. Here, we summarise the extended model of DSSCs that also include the effect of electrolyte concentrations. This model allows insights into the distribution of charged particles in DSSCs beyond the nanoporous semiconductor.

The earliest model in this area was published in 1996 by Papageorgiou et al.\[60\]. Although this model does not consider the influence of electrons in the conduction band on the electrolytes, it provides the framework for such extension, which is investigated by Andrade et al.\[1\]. In [1], the iodide-triiodide electrolyte couple is modelled by the following diffusion equations:

\[
\begin{align*}
D_{i_1} \frac{\partial^2 n_{i_1}}{\partial x^2} - \frac{3}{2} \left[ \eta \phi \alpha \phi \alpha - \frac{n_e(x, t) - n_{eq}}{\tau_e} - \frac{\partial n_e}{\partial t} \right] &= \frac{\partial n_{i_1}}{\partial t}, \\
D_{i_2} \frac{\partial^2 n_{i_2}}{\partial x^2} + \left[ \eta \phi \alpha \phi \alpha - \frac{n_e(x, t) - n_{eq}}{\tau_e} - \frac{\partial n_e}{\partial t} \right] &= \frac{\partial n_{i_2}}{\partial t},
\end{align*}
\]

where \( n_{i_1} \) and \( n_{i_2} \) are the densities of the iodide and triiodide, respectively, \( D_{i_1} \) and \( D_{i_2} \) are the diffusion coefficients of the iodide and triiodide and \( \phi \) is the porosity of TiO\(_2\). The accompanying initial and boundary conditions result from assuming a given initial concentration, a net flux of zero at the TCO electrode and a constant total concentration throughout the operation\[1\]. Mathematically, we can express these conditions as

\[
\begin{align*}
n_{i_1}(x, 0) &= n_{i_1}^{init}, \\
n_{i_2}(x, 0) &= n_{i_2}^{init}, \\
\frac{\partial n_{i_1}}{\partial x} &\bigg|_{x=0} = 0, \\
\frac{\partial n_{i_2}}{\partial x} &\bigg|_{x=0} = 0, \\
\int_0^d n_{i_1}(x, t) \, dx &= dn_{i_1}^{init}, \\
\int_0^d n_{i_2}(x, t) \, dx &= dn_{i_2}^{init},
\end{align*}
\]

where \( n_{i_1}^{init} \) and \( n_{i_2}^{init} \) are respectively the initial concentrations of the iodide and triiodide.

So far, this is the only model for the electrolyte couple under pure diffusion, and is used in a number of papers, such as [1, 25, 35, 55].

2.6. Current-voltage relationship

The purpose of modelling electron density by diffusion is to use the computed conduction band electron density to determine the current-voltage relationship in DSSCs. From there, we may calculate efficiency. Included with the diffusion model given by Södergren et al.\[36\], the paper also provides the derivation of the \( J - V \) characteristics of a DSSC based on the diode equation.
The diode equation for current \( I \) as a function of voltage \( V \) is given by

\[
J(V) = J_{sc} - J_0 \left( e^{\frac{qV}{n_0k_BT}} - 1 \right),
\]

where \( J_{sc} \) is the short-circuit current density, \( J_0 \) is the reverse saturation coefficient, \( q \) is the electron charge, \( n_0 \) is the ideality factor, \( k_B \) is Boltzmann’s constant and \( T \) is the temperature of the DSSC. By construction \( J(0) = J_{sc} \).

Likewise, we define the open-circuit voltage \( V_{oc} \) to be the solution to \( J(V_{oc}) = 0 \).

We obtain the short-circuit current density \( J_{sc} \) and the open-circuit voltage \( V_{oc} \) from the electron density \( n(x) \), which is the solution to the diffusion equation:

\[
D_0 \frac{d^2n}{dx^2} + \phi \alpha e^{-\alpha x} - \frac{n(x) - n_0}{\tau} = 0,
\]

under the boundary conditions given in section 2.1. The photocurrent density \( J \) is given by [61]

\[
J = qD_0 \frac{\partial n}{\partial x} \bigg|_{x=0},
\]

where \( q \) is the electron charge. As the short-circuit current density \( J_{sc} \) is found by this equation under short-circuit conditions (in which the bias voltage \( V = 0 \) for the electron density \( n_{oc} \)), this yields the expression [35]

\[
J_{sc} = qD_0 \frac{\partial n_{oc}}{\partial x} \bigg|_{x=0} = \frac{q\phi \alpha L \left( -L \alpha \cosh\left( \frac{d}{L} \right) + \sinh\left( \frac{d}{L} \right) + \alpha L e^{-\alpha d} \right)}{(1 - L^2 \alpha^2) \cosh\left( \frac{d}{L} \right)},
\]

(33)

where \( L = \sqrt{D_0 \tau} \) is the electron diffusion length. The open-circuit voltage is found by solving equation (8) under the alternative boundary condition \( \frac{\partial n}{\partial x} \bigg|_{x=0} = 0 \) to find the open-circuit electron density \( n_{oc} \). Therefore, the open-circuit voltage is found by

\[
V_{oc} = \frac{m_k T}{q} \ln \left[ \frac{n_{oc}(0)}{n_0} \right] = \frac{m_k T}{q} \ln \left( 1 + \frac{\phi \alpha \tau \left( \alpha L \cosh\left( \frac{d}{L} \right) - \alpha L e^{-\alpha d} - \sinh\left( \frac{d}{L} \right) \right)}{n_0 (L^2 \alpha^2 - 1) \sinh\left( \frac{d}{L} \right)} \right).
\]

(34)

Using the expressions for \( J_{sc} \) and \( V_{oc} \), we obtain the dark saturation current density as given by Södergren et al [36] as

\[
J_0 = \frac{J_{sc}}{e^{\frac{qV_{oc}}{n_0k_BT}}} - 1 = \frac{qD_0 n_0}{L} \tanh\left( \frac{d}{L} \right).
\]

2.7. Efficiency

The performance of DSSCs can be determined from the efficiency of the devices. The efficiency \( \eta \) is defined as [62]

\[
\eta = \frac{J_{sc} V_{oc} \text{FF}}{P_{in}} = \frac{P_{max}}{P_{in}} = \frac{V_{max} J_{max}}{P_{in}},
\]

(35)

where \( P_{in} \) is the total power available from sunlight. For the AM1.5 solar spectrum, \( P_{in} \) is taken to be 1000 Wm\(^{-2}\) [63]. We calculate power by the standard formula \( P = IV \), which takes the form

\[
P(V) = VJ(V) = V \left[ J_{sc} - J_0 e^{\frac{qV}{n_0k_BT}} \right].
\]

(36)

To find the maximum power point \( (V_{max}, J_{max}) \), we optimise \( P \) over \( V \) to obtain \( V_{max} \) and then compute \( J_{max} = J(V_{max}) \). Differentiating both sides of equation (36) with respect to \( V \), we obtain

\[
\frac{dP}{dV} = J_{sc} + J_0 e^{\frac{qV}{n_0k_BT}} \left[ \frac{qV}{m_k T} + 1 \right],
\]

\[
\frac{d^2P}{dV^2} = -\frac{qJ_0}{m_k T} \left[ \frac{qV}{m_k T} + 2 \right].
\]

As all parameters in the expression for \( \frac{d^2P}{dV^2} \) are positive, we get \( \frac{dP}{dV^2} < 0 \) for all voltages \( V \in [0, V_{oc}] \). Thus, all critical points will be maximum values in this domain. Using the Lambert -W function, we obtain an explicit expression for the maximum power point, given by
\[
V_{\text{max}} = \frac{m k_b T}{q} \left[ W \left( e \frac{J_c}{J_0} \right) - 1 \right], \\
J_{\text{max}} = \frac{(J_c + I_0) W \left( e \frac{J_c + h}{h} \right) - 1}{W \left( e \frac{J_c}{h} \right)}.
\]

Therefore, the maximum power output of the DSSC is given by
\[
P_{\text{max}} = P(V_{\text{max}}) = \frac{m k_b T (J_c + I_0) W \left( e \frac{J_c + h}{h} \right) - 1}{q W \left( e \frac{J_c}{h} \right)}.
\]

We compute the short-circuit current density \( J_{sc} \) and the open-circuit voltage \( V_{oc} \) under each model by using the expressions given in equations (33) and (34). In section 4, we calculate efficiencies for DSSCs using these equations.

### 2.8. Incident photon to current efficiency

In addition to efficiency \( \eta_i \), the incident photon to current efficiency (IPCE) curve can be used to gauge the performance of DSSCs with regard to photons of a particular wavelength. While it is used as a performance indicator, the short-circuit current density \( J_c \) may be calculated using the IPCE(\( \lambda \)) by [6]
\[
J_c = \frac{h c}{q} \int \lambda \text{IPCE}(\lambda) \phi(\lambda) d\lambda,
\]
where \( h \) is Planck’s constant, \( c \) is the speed of light, \( q \) is the electron charge and \( \phi \) is the incident radiative flux. There are several definitions for IPCE(\( \lambda \)). The first definition is directly from O’Regan and Grätzel [4],
\[
\text{IPCE}(\lambda) = \text{LHE}(\lambda) \phi_{inj} \eta_i,
\]
where LHE(\( \lambda \)) is the wavelength dependent light harvesting efficiency, \( \phi_{inj} \) is the electron injection efficiency (also denoted by \( \eta_i \)) and \( \eta_i \) is the electron collection efficiency.

An alternative definition for IPCE(\( \lambda \)) is given in Tanaka [59],
\[
\text{IPCE}(\lambda) = \frac{h c J_c}{q \lambda \phi(\lambda)},
\]
where \( J_c \) is the short-circuit current density and \( \phi \) is the incident radiative flux.

We note that the quantity \( h c / q \) is often replaced by the numerical value 1240 [3, 14] or 1239 [64]. This value is obtained from converting \( h, c \) and \( q \) to SI units, i.e.
\[
\frac{h c}{q} \approx 1240 \text{ kgm}^2\text{nms}^{-3}\text{A}^{-1}.
\]

Finally, Barnes and O’Regan [48] define IPCE(\( \lambda \)) as [48]
\[
\text{IPCE} = -\frac{D_0}{\phi} \frac{\partial n_c}{\partial x} \bigg|_{x=0},
\]
where \( D_0 \) is the diffusion constant for electron density in the DSSC, \( \phi \) is the incident radiative flux and \( n_c \) is the conduction band electron density of the DSSC.

### 3. Electron diffusion equation

#### 3.1. Nondimensional model

Consider a special case of equation (8) as studied by Anta et al [40]. That is, suppose \( D(n) = D_0 \left( \frac{n}{n_{eq}} \right)^\beta \),
\[
G(x) = \varphi c e^{-\alpha x} \text{ and } R(n) = k_b \left[ \frac{n}{n_{eq}} \right]^\beta (n - n_{eq}).
\]
Using the change of variables \( \tilde{n} = \frac{n}{n_{eq}}, \tilde{x} = \frac{x}{\bar{d}}, \text{ and } \tilde{t} = \frac{D_0 t}{\bar{d}^2} \), we can rewrite the diffusion equation as
\[
\frac{\partial \tilde{n}}{\partial \tilde{t}} = \frac{\partial}{\partial \tilde{x}} \left[ \tilde{D}^\beta \frac{\partial \tilde{n}}{\partial \tilde{x}} \right] + \mu e^{-\nu x} - \xi \tilde{n}^\beta [\tilde{n} - 1],
\]
where \( \mu = \frac{d^2 \varphi c}{D_0 n_{eq}}, \nu = \alpha \bar{d} \text{ and } \xi = \frac{k_b \bar{d}^2}{D_0} \) are our nondimensional constants. Under short-circuit conditions, the boundary conditions become
where

\[ w = qV_{mk TB}. \]

Using the values of parameters given in Anta et al [40] and Gacemi et al [35], we obtain the values of nondimensional constants \( \mu, \nu \) and \( \xi \) for the nonlinear diffusion equation as shown in table 3.

3.2. Linear special case

Assuming \( \beta = 0 \), \((39)\) reduces to a linear PDE which has an analytical solution (provided by Maldon et al in their 2020 paper [5]). The analytical solution is given by

\[ n(x, t) = 1 + Ae^{\sqrt{\xi}x} + Be^{-\sqrt{\xi}x} - \frac{\mu}{\nu^2 - \xi} e^{-\nu t} + \sum_{k=0}^{\infty} C_k \sin \left( \frac{(2k + 1) \pi}{2} x \right) e^{\left( (\xi + 1) - \sqrt{(\xi + 1)^2 - 4\xi} \right)}, \]

(41)

where \( \omega = \frac{qV}{mkB} \).

Using the values of parameters given in Anta et al [40] and Gacemi et al [35], we obtain the values of nondimensional constants \( \mu, \nu \) and \( \xi \) for the nonlinear diffusion equation as shown in table 3.

**Figure 6.** Exact solution \( n(x, t) \) for \((41)\) under short-circuit conditions (left) and open-circuit conditions (right).

**Table 3.** Parameter values for DSSC model and our calculated nondimensional parameters.

| Parameter | Value | References |
|-----------|-------|------------|
| \( D_0 \) | \( 2 \times 10^{-9} \text{ m}^2\text{s}^{-1} \) | [37] |
| \( \alpha \) | \( 5 \times 10^3 \text{ m}^{-1} \) | [37] |
| \( d \) | \( 10^{-5} \text{ m} \) | [35] |
| \( k_d \) | \( 42.37 \text{ s}^{-1} \) | [1] |
| \( n_{eq} \) | \( 10^{22} \text{ m}^{-3} \) | [38] |
| \( \varphi \) | \( 10^{21} \text{ m}^{-3} \text{s}^{-1} \) | [37] |
| \( \mu \) | 2500 | — |
| \( \nu \) | 5 | — |
| \( \xi \) | 2.118 | — |

Unlike other existing solutions in the literature (such as that of [22]), equation \((41)\) not only presents the nondimensional solution but also incorporates bias voltage \( V \) despite the majority of papers considering only short-circuit conditions (such as [1] and [65]).

In figure 6, we plot this solution under short-circuit conditions using 100 terms of the infinite series for \( x \in [0, 1] \), \( t \in [0, 1] \) and the parameters given in table 3.
3.3. Nonlinear case
Based on the Lie symmetry analysis carried out by Maldon \textit{et al} in their 2020 paper, we find that physically relevant versions of the nonlinear PDE (39) do not exhibit symmetry solutions [5]. Thus, we solve this equation numerically, as shown in [40, 66]. In [67], we solve equation (39) with the boundary conditions (40) using a forward time continuous space finite difference scheme. All simulations use 100 spatial nodes and 100,000 temporal nodes with constant values taken from table 3.

In figure 7, we see that the numerical solution greatly resembles the exact solution for the linear case, suggesting that nonlinear diffusion only affects the overall magnitude of the solution. Nevertheless the nonlinear diffusion coefficient significantly lowers the overall electron density, corresponding to stronger traps in the TiO$_2$ semiconductor [68].

3.4. Effect of parameters on electron density
We investigate the effect of the parameters $\mu$, $\nu$ and $\xi$ on the solution profile for the linear case $\beta = 1$ as given by (39).

In figure 8, we plot the numerical solution for $t = 1$ for the electron density to elucidate the effect of $\beta$. We see that higher values of $\beta$ lead to an overall decrease in electron density. Furthermore, numerical solutions reach an equilibrium faster with increased values for $\beta$. Given that $\beta$ governs the density of trap states in a DSSC.
(higher values of $\beta$ leading to deeper traps [40]), this result shows that the nonlinear diffusion mechanism is functioning in equation (39) as expected.

Figure 9 shows the relationship between $\mu$ and the electron density. By varying $\mu$ by several powers of 10, we see that the increase in values of $\mu$ leads to a significant overall increase in electron densities. This is as expected since $\mu$ is the main coefficient in the source term $m = n - Ge^x$.

Next, we consider the effect of $\nu$ on the electron density. For this study, we run simulations varying values of $\nu$ by different multiples of the original value in table 3. Since $G(x) = \mu e^{-\beta x}$, an increase in $\nu$ leads to a decrease in the electron generation, which in turn decreases the electron density as we see in figure 10.

Finally, figure 11 demonstrates the effect of the recombination parameter $\xi$ on the electron density. The increased values of $\xi$ correspond to higher levels of recombination, which is reflected in figure 11 as the electron density decreases for higher values of $\xi$. 

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**Figure 9.** Plot of $n(x, 1)$ for various values of $\mu$.

**Figure 10.** Plot of $n(x, 1)$ for various values of $\nu$. 

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4. Efficiencies

According to data provided in each reference shown in table 4, we compute the nondimensional parameters $\mu$, $\nu$ and $\xi$ of the DSSC model. The extreme values for $\mu$ are primarily due to the high values of the incident photon flux $f$ and the low values of the diffusion coefficient $D$. Discrepancies between the values of $\mu$ in table 4 are largely due to the value used for the dark equilibrium electron density, $n_{eq}$. In Andrade et al [1], $n_{eq}$ is given by

$$n_{eq} = n_0 e^{-\frac{E_c - E_{Redox}}{kT}},$$

where $n_0$ is the effective density of states in the DSSC, $E_c$ is the conduction band energy and $E_{Redox}$ is the redox energy of the DSSC. Given that $n_0 = 10^{27}$ m$^{-3}$, $E_c - E_{Redox} = 0.93$ eV and $T = 298$ K, we find $n_{eq} \approx 1.87 \times 10^{11}$ m$^{-3}$.

Alternatively, Ni et al [39] assumes that the electron density is of the order $10^{22}$ m$^{-3}$. This distinction primarily affects the open-circuit voltage $V_{oc}$, which in turn affects efficiency $\eta$.

Table 5 shows the computed efficiency of the DSSC according to the data found for each reference. Given O’Regan and Grätzel’s [4] original DSSC featured an efficiency of 7.1–7.9%, we find that the values for efficiency in table 5 generally underestimate the measured efficiency of DSSCs. In most cases, this is due to an underestimation of the short-circuit current density, given as $\approx 120$ Am$^{-2}$ by O’Regan and Grätzel [4]. Nevertheless, values for the open-circuit voltage are in good agreement with the literature, with O’Regan and Grätzel’s benchmark of $V_{oc} \approx 0.7$ V.

| Author          | References | $\mu$     | $\nu$     | $\xi$  |
|-----------------|------------|-----------|-----------|--------|
| Ni et al (2006) | [39]       | 250       | 5         | 0.5    |
| Andrade et al (2011) | [1]       | $7.292 \times 10^{12}$ | 1         | 0.385  |
| Gacemi et al (2013) | [35]      | $4.861 \times 10^{12}$ | 1         | 0.385  |
| Shi et al (2013) | [51]       | $6.417 \times 10^{11}$ | 4         | 2.5    |
| Lopes et al (2015) | [25]      | $2.483 \times 10^{10}$ | 1.25      | 0.602  |
| Belarbi et al (2015) | [15]     | $4.327 \times 10^{12}$ | 1         | 0.385  |

Figure 11. Plot of $n(x, 1)$ for various values of $\xi$. 

Table 4. Nondimensional parameter values for various DSSC diffusion models.
5. Summary

In summary, we have reviewed the diffusion model for DSSCs. Modelling DSSC performance on the density of charge carriers is largely inherited from previous knowledge of solar cells but is known to be a diffusion-dominated process [22, 33].

From the electron density we calculate the short-circuit current density $J_s$, the open-circuit voltage $V_{oc}$ and the efficiency $\eta$ of a DSSC based on the diode equation. Our results for electron density are in good agreement with the literature. We analyse the electron density as a solution to equation (8) under variation in the nondimensional parameters $\mu$, $\nu$ and $\xi$ and provide their typical values based on data given in the literature. Although some values are in line with literature benchmarks, there is plenty of scope for improvement. Few DSSC models consider the impact of the electrolytes and the counter electrode on the overall electron density. Moreover, these models additionally opt for steady-state measurements. To improve DSSC models, we suggest expanding the PDE given by (8) to include the effect of the counter electrode and the electrolytes. Finally, given the fractal geometry of the nanoporous semiconductor TiO$_2$, we also suggest a fractional diffusion equation in a similar vein to Nigmatullin [69].

Acknowledgments

The authors acknowledge the support of the Australian Government Research Training Program Scholarship for BM. The authors are also grateful to the Australian Research Council for the funding of Discovery Project DP170102705.

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