1 Introduction

The search for sustainable, inexpensive and environmentally friendly energy has led researchers to the development of photovoltaic devices that directly convert sunlight into usable electrical power. At present, commercially produced photovoltaic cells are generally solid–state, p–n junction devices such as silicon based solar cells. These solar cells are usually expensive to manufacture [6]. Photoelectrochemical cells, such as Dye–Sensitised Solar Cells (DSCs), provide an inexpensive alternative to present day p–n junction photovoltaics and consist of a semiconductor–electrolyte junction rather than a solid–state junction. Presently DSCs are about 7–11% efficient [5], and it is thought that if commercially produced DSCs can reach an efficiency of more than 12%, then energy production would be at a significantly lower cost than the current cost of alternative photovoltaic devices.

In this work we present a mathematical model of the semiconductor–electrolyte interface in a DSC under non-illuminated conditions in order to investigate and understand the importance of the dark current as a loss mechanism for such a cell.

The basic structure of a DSC can be divided into three main parts (see Figure 1), the nanoporous dye–sensitised semiconductor, the electrolyte solution, and the transparent conducting electrodes. The nanoporous semiconductor has a large internal surface area and is usually made up of sintered anatase titanium dioxide (TiO$_2$) particles. The semiconductor is coated with a monolayer of light absorbing dye capable of charge transfer. The dye coated TiO$_2$ electrode is flooded with a redox couple in solution, the electrolyte. An example of this electrolyte is an organic, iodide (I$^-$) and triiodide (I$_3^-$), solution. This TiO$_2$–dye–electrolyte assembly is sandwiched between two glass plates coated with layers of a transparent conductive oxide (TCO), for example tin oxide (SnO$_2$).

Upon illumination of the cell, dye molecules, S, absorb light (photons of an appropriate wavelength) and are excited to a new state, $S^*$. The excited molecules inject electrons, at a high rate, into the conduction band of the TiO$_2$ semiconductor, and the molecules of dye become cations, $S^+$. The electrons in the TiO$_2$ diffuse through the solid to the glass electrode and work is done by an external load, yielding usable energy. The electrons then move to the counter electrode where they reduce the redox species via the reaction $I^- + 2e^- \rightarrow 3I^-$. The $I^-$ ions are transported through the electrolyte solution and eventually contact the cationic dye molecules. The $I^-$ ions are then oxidised in a reaction that returns the cationic dye molecules to their ground state, namely, $S^+ + e^- \rightarrow S$.

There are a number of loss mechanisms that limit the current produced by a DSC. These include loss mechanisms at the interface. For example, the semiconductor surface is not completely covered with dye and non-dye reactions between the electrolyte and TiO$_2$ occur. These reactions do not require the presence of photons in order to occur and the current aris-
ing from them, referred to as the dark current, can be opposite in sense to the operating current of the cell. Furthermore, we note that the kinetics of these non-dye reactions at the semiconductor–electrolyte interface will be an important factor in determining their significance as a loss mechanism. This is emphasised by the fact that there is no depletion layer in the semiconductor [6] due to the nano-sized particles. As a consequence there are no electron–hole pairs created in the semiconductor from illumination and the current produced by the solar cell depends on the rate of transfer of holes or electrons to the electrolyte.

1.1 Previous Work There have been a number of attempts to model the semiconductor–electrolyte interface in a DSC or a conventional solar cell. Gerischer [4] provides a model for the cathodic and anodic currents across the conduction band and valence band of a semiconductor–electrolyte interface. The interface is modelled as a single plane and simplifying assumptions are made concerning the concentrations of the redox couple in solution, the holes in the conduction band, the electrons in the valence band and the electrons in the bulk of the semiconductor.

Ferber et al. [2], Ferber and Luther [3] and Stangl et al. [10], present a simplified model of a complete DSC. These models incorporate only one electron loss mechanism at the semiconductor–electrolyte interface.

Orazem and Newman [8] present a mathematical model for a gallium arsenide (GaAs) liquid–junction photovoltaic cell. Macroscopic transport equations for the semiconductor and the electrolyte bulk are coupled to a microscopic model of the semiconductor–electrolyte interface. The interface model is based on the diffuse double–layer theory, (see for example [1, 4]), and includes all of the possible reactions involving the ionic species in the electrolyte and/or the electrons and holes in the semiconductor, and it is in this way that this model differs from others presented in the literature. Due to the difficulty in measuring the kinetic parameters at the interface, simplifying assumptions have been made concerning the form and value of the rate constants involved in the model. In a second paper, Orazem and Newman [9] validate their model by comparing their numerical results to experimental results. These comparisons show that cell performance is influenced by, among other things, the kinetics of the interfacial reactions.

In the present work we will develop a mathematical model of the semiconductor–electrolyte interface, devoid of any dye, and we analyse the non-photon mediated or ‘dark current’ reactions only. We also assume that the interface is isothermal.

2 Development of Model Equations

2.1 The Semiconductor–Electrolyte Interface In an approach similar to that of Orazem and Newman [8], we consider a detailed semiconductor–electrolyte interface where the electrical double layer formed at the interface is split into distinct regions. The term ‘electrolyte semiconductor interface’ is split into distinct regions. The term ‘electrochemical double layer’ refers to the region of charge separation which is formed at the interface [1]. The current across the double layer will be made up of a number of different reactions, with each reaction depending on the region in which it occurs. The interface is assumed to exist at a single point, having no appreciable length.

We have identified 11 non-photon mediated reactions that occur at the semiconductor–electrolyte interface of the DSC. These reactions, along with the assumed structure of the double layer, are shown schematically in Figure 2. We note that the forward direction chosen for each reaction is the movement of electrons and electrolyte species into or towards the semiconductor, and furthermore, each of these reactions is assumed to be reversible.

On the solution side of the interface, we assume that the double layer is made up of the Outer Helmholtz Plane (OHP) and the Inner Helmholtz Plane (IHP) [1]. The OHP is the plane of closest approach of non-specifically adsorbed ions in the electrolyte solution. The IHP is located at the electrical centre of specifically adsorbed ions that have lost their solvation sheath in moving from OHP to IHP. Reactions 4 and 5 in Figure 2 represent these desolvating–solvating reactions.

The semiconductor side of the interface is assumed to consist of the Inner Surface States (ISS) and the Outer Surface States (OSS). The OSS represents the plane of closest approach for electrons and holes that are associated with the bulk semiconductor. At this plane, high and low energy levels of charges are considered and these energy levels represent the bottom of the conduction band (CB) and the top of the valence band (VB), respectively. The ISS is the plane of surface sites for adsorbed electrons and holes from the bulk semiconductor. As with the OSS, a high energy, or CB site, and a low energy, or VB site, is considered at the ISS. However, in addition to these sites we consider the existence of surface trap sites \(t\) at the ISS. A physical interpretation of \(t\) sites is given by noting that at the ISS there are flaws in the crystal causing dangling bonds in the lattice creating trap sites for...
electrons, and that these sites usually have energy levels between the CB and the VB. Reactions 6, 7 and 8 describe the movement of charged species between the CB of the OSS and the CB, VB and VB energy states of the ISS, respectively. Reactions 9, 10 and 11 describe the movement of charged species between the VB of the OSS and the VB, CB and CB states of the ISS respectively.

The oxidation and reduction of ionic species in the electrolyte occurs via reactions 1, 2 and 3. An example of these reactions, in the forward direction, is reaction 1 where the IHP oxidant species gives off an electron, or electrons, into the CB energy state of the ISS and is itself reduced to an IHP oxidant.

Modelling the interface in this amount of detail allows important information about the surface of the semiconductor and electrolyte to be included, such as the presence of trap sites and the kinetics of charge transfer. However, the downside to such a detailed model is that a large amount of parameter estimation is required.

2.2 Current and Rate Equations

In this section we will develop the kinetic equations that relate the interfacial currents to the interfacial potential gradients.

We begin by considering the general electrode reaction [7],

\[ b \text{ Red} + n h = a \text{ Ox} + ne^-, \]

which we will assume is taking place at a semiconductor-electrolyte interface. Here Ox and Red represent the oxidant and reductant respectively, e\(^-\) represents electrons, h represents vacant sites, or holes, in the semiconductor, a, b, and n are stoichiometric coefficients and \(k_f\) and \(k_b\) are the rate constants for the forward (anodic) and backward (cathodic) reactions respectively. The total current density, \(i\) (A/cm\(^2\)), associated with reaction 1 is given by the forward current density, \(i_f\) (A/cm\(^2\)), minus the backward current density, \(i_b\) (A/cm\(^2\)), namely [1],

\[ i = nF \left( k_f [\text{Red}]^b [h]^n - k_b [\text{Ox}]^a [e^-]^n \right), \]

where [ ] denotes concentration. We now assume that the rate constants, \(k_f\) and \(k_b\), have an Arrhenius form [1] that can be expressed as,

\[ k_f = A_f \exp \left[ \frac{-\Delta G_f}{RT} \right], \]

and

\[ k_b = A_b \exp \left[ \frac{-\Delta G_b}{RT} \right], \]

where \(\Delta G_f\) and \(\Delta G_b\) (J/mol) are the standard free energies of activation for oxidation and reduction respectively, \(A_f\) and \(A_b\) are frequency factors, \(R\) (J/K/mol) is the molar gas constant and \(T\) (K) is temperature. The potential dependence of the standard cathodic and anodic activation energies is given by [1],

\[ \Delta G_c = \Delta G_c^0 + \beta nF \Delta \phi, \]

and

\[ \Delta G_a = \Delta G_a^0 - (1 - \beta)nF \Delta \phi, \]

respectively. Here \(\Delta G_f^0\) and \(\Delta G_b^0\) (J) are the cathodic and anodic activation energies at a known reference, respectively, the potential \(\Delta \phi\) (V) is the difference in potential between the solid and solution and \(\beta\) is the transfer coefficient, usually taken as one half. Combining (3), (4), (5) and (6) with (2) and denoting the pre-exponential components of the forward and backward rate constants as \(k_f^0\) and \(k_b^0\), respectively, the overall current is given by [7]

\[ i = nF \left( k_f^0 [\text{Red}]^b [h]^n \exp \left[ (1 - \beta)nF \Delta \phi \right] \right) - k_b^0 [\text{Ox}]^a [e^-]^n \exp \left[ -\beta nF \Delta \phi \right], \]

where \(f = F/RT\).

Using (7) we express the equilibrium potential, \(\phi^0\), as a function of species concentrations and the rate constants, namely,

\[ \phi^0 = -\frac{1}{nF} \ln \frac{k_f^0 k_b^0}{k_b^0 [\text{Ox}]^a [e^-]^n} + \ln \frac{[\text{Red}]^b [h]^n}{[\text{Ox}]^a [e^-]^n} \]

Furthermore “at a given reference state” (8) becomes,

\[ \phi_{\text{ref}}^0 = -\frac{1}{nF} \ln \frac{k_f^0 k_b^0}{k_b^0 [\text{Ox}]^a [e^-]^n} + \ln \frac{[\text{Red}]_{\text{ref}}^b [h_{\text{ref}}]^n}{[\text{Ox}_{\text{ref}}]^{a_{\text{ref}}} [e_{\text{ref}}^-]^n}, \]

were the subscript \(\text{ref}\) denotes values measured at the reference state.

At equilibrium we may set \(i_f = i_b = i_0\), where \(i_0\) (A/cm\(^2\)) is the exchange current density, given by,

\[ i_0 = nFk_f^0 [\text{Red}]^b [h]^n \exp \left[ (1 - \beta)nF \phi^0 \right] = nFk_b^0 [\text{Ox}]^a [e^-]^n \exp \left[ -\beta nF \phi^0 \right]. \]

Combining (8) and (10) we may obtain an expression for \(i_0\), namely,

\[ i_0 = nF \left( k_f^0 [\text{Red}]^b [h]^n \right) \beta \left( k_b^0 [\text{Ox}]^a [e^-]^n \right)^{1 - \beta}. \]

Combining (7), (8), (9) and (11) we obtain an expression for the total current across a semiconductor-electrolyte interface written with respect to a reference exchange current density, namely,

\[ i = nF \left( [\text{Red}]^b [h]^n \right) \lambda_1 (\Delta \phi - \phi_{\text{ref}}^0) - \left( [\text{Ox}]^a [e^-]^n \right) \lambda_2 (\Delta \phi - \phi_{\text{ref}}^0), \]

where

\[ \lambda_1 (\Delta \phi - \phi_{\text{ref}}^0) = \exp \left[ (1 - \beta)nF (\Delta \phi - \phi_{\text{ref}}^0) \right] \]

and

\[ \lambda_2 (\Delta \phi - \phi_{\text{ref}}^0) = \exp \left[ -\beta nF (\Delta \phi - \phi_{\text{ref}}^0) \right], \]

and the reference exchange current density is given by

\[ i_{\text{ref}}^0 = nF \left( k_f^0 [\text{Red}_{\text{ref}}]^b [h_{\text{ref}}]^n \right) \beta \times \left( k_b^0 [\text{Ox}_{\text{ref}}]^{a_{\text{ref}}} [e_{\text{ref}}^-]^n \right)^{(1 - \beta)}. \]
3 The Complex Model

We now apply Equation (12) to each of the reactions in our double-layer structure as indicated in Figure 2. We begin by considering the reactions between the OHP and the IHP. We assume that the only species present in solution are the oxidant and reductant and that a constant number of sites, \( \Gamma_{ihp} \) (mol/cm\(^3\)), are available for the adsorbed species at the IHP. In addition, we assume that an OHP oxidant species, \( \text{O}_{\text{ox,ihp}} \), or reductant species, \( \text{Red}_{\text{ihp}} \), will only be adsorbed onto the IHP, to yield \( \text{O}_{\text{ox,ihp}} \) or \( \text{Red}_{\text{ihp}} \), respectively, for a particular reaction. Thus when electrons and holes at the OSS, \( \text{e}_{\text{iss}} \) and \( \text{h}_{\text{iss}} \), are driven by a potential gradient alone, how-ever, we acknowledge that this may not be the only transport process involved in the adsorption of solution species onto the IHP. Diffusion may play a role and may even dominate this process [1]. This will be a focus of further work by the authors.

Applying equation (12) to reaction (16) we obtain the transfer current, \( i_4 \) (A/cm\(^2\)), generated by the reaction, namely,

\[
i_4 = i_{4,\text{ref}}^0 \left( \frac{C_{\text{ox}} [\Gamma_{\text{ihp}} - \sum_i \gamma_i]}{C_{\text{ox,ref}} [\Gamma_{\text{ihp}} - \sum_i \gamma_{i,\text{ref}}]} \times \lambda_1 (\Delta \phi_4 - \phi_{4,\text{ref}}^0) \right) - \frac{[\gamma_{\text{ox}}]}{[\gamma_{\text{ox,ref}}]} \lambda_2 (\Delta \phi_4 - \phi_{4,\text{ref}}^0) .
\]

Here, \( \Delta \phi_4 = \phi_{\text{iss}} - \phi_{\text{ihp}} \) (V) is the potential difference between the OHP and the IHP, \( C_{\text{ox}} \) and \( C_{\text{red}} \) (mol/cm\(^3\)) are the concentrations of oxidant and reductant at the OHP respectively, \( \gamma_{\text{ox}} \) and \( \gamma_{\text{red}} \) (mol/cm\(^3\)) are the concentrations of oxidant and reductant at the IHP respectively, and \( [\Gamma_{\text{ihp}} - \sum_i \gamma_i] \) (mol/cm\(^3\)) is the concentration of vacant sites at the IHP. A similar expression for the current, \( i_5 \) (A/cm\(^2\)), exists for reaction 5. We note that here we have assumed that reactions 4 and 5 are driven by a potential gradient alone, however, we acknowledge that this may not be the only transport process involved in the adsorption of solution species onto the IHP. Diffusion may play a role and may even dominate this process [1]. This will be a focus of further work by the authors.

Between the IHP and ISS we consider the three electrochemical reactions represented by the general expression,

\[
b \text{Red}_{\text{ihp}} + n \text{O}_{\text{ox,ihp}} \xrightleftharpoons[]{} k_{\text{f,l}} \text{Red}_{\text{zos}} + n \text{O}_{\text{ox,zos}}.
\]

Here the subscript \( l \) designates the particular reaction under investigation. The value of \( l \) in expression (18) will be either 1, 2 or 3, where these labels coincide with those used to label the reactions in Figure 2. The superscript \( i \) in the expression (18) designates the energy state which acts as the source of the electrons and holes at the ISS, \( e_{\text{iss}} \) and \( h_{\text{iss}} \) respectively, for a particular reaction. Thus when \( l = 1, i = cb; \) when \( l = 2, i = t; \) and when \( l = 3, i = vb \). Applying equation (12) to the reactions in (18) we obtain the transfer current densities generated by the reactions between the IHP and ISS, namely,

\[
i_l = i_{l,\text{ref}}^0 \left( \frac{[\gamma_{\text{ox}}]}{[\gamma_{\text{ox,ref}}]} [\Gamma_{\text{iss}} - \Gamma_{\text{ss}}] \times \lambda_1 (\Delta \phi_2 - \phi_{2,\text{ref}}) \right) - \frac{[\gamma_{\text{ox}}]}{[\gamma_{\text{ox,ref}}]} \lambda_2 (\Delta \phi_2 - \phi_{2,\text{ref}}) .
\]

Here \( \Delta \phi_2 = \phi_{\text{iss}} - \phi_{\text{ihp}} \) (V), is the potential difference between the ISS and the OSS, \( C_{\text{ox}} \) (mol/cm\(^3\)) is the concentration of electrons at the OSS energy state \( i \) and \( \Gamma_{\text{iss}} \) (mol/cm\(^3\)) is the total site concentration for energy state \( i \) at the ISS. Furthermore, assuming that the only species present at the ISS are \( e_{\text{iss}} \) and \( h_{\text{iss}} \) and that a hole is formed by the absence of an electron, then \( [\Gamma_{\text{iss}} - \Gamma_{\text{ss}}] \) (mol/cm\(^3\)) represents the concentration of holes at the ISS energy state \( i \). Between the ISS and OSS we consider the electrochemical reactions represented by the general expression,

\[
e_{\text{iss}} + h_{\text{iss}} \xrightleftharpoons[]{} k_{\text{f,l}} a \text{O}_{\text{ox,iss}} + n \text{e}_{\text{iss}}.
\]

Here the meaning of \( l \) is analogous to that given previously for reactions between the IHP and the ISS and we note that, in accordance with Figure 2, the value of \( l \) in expression (20) will be either 6, 7, 8, 9, 10 or 11. Furthermore, when \( l = 6 \) or 11, \( i = cb; \) when \( l = 7 \) or 10, \( i = t; \) when \( l = 8 \) or 9, \( i = vb \). In addition, we note that the superscript \( j \) in expression (20) designates the energy state which acts as the source of electrons and holes at the OSS, \( e_{\text{oss}} \) and \( h_{\text{oss}} \) respectively, for a particular reaction. Thus when \( l = 6, 7, 8, j = cb \) and when \( l = 9, 10, 11, j = vb \). Applying Equation (12) to the reactions in (20) we obtain the transfer current densities for the reactions between the ISS and OSS, namely,

\[
i_l = i_{l,\text{ref}}^0 \left( \frac{[\gamma_{\text{ox}}]}{[\gamma_{\text{ox,ref}}]} [\Gamma_{\text{iss}} - \Gamma_{\text{ss}}] \times \lambda_1 (\Delta \phi_3 - \phi_{3,\text{ref}}) \right) - \frac{[\gamma_{\text{ox}}]}{[\gamma_{\text{ox,ref}}]} \lambda_2 (\Delta \phi_3 - \phi_{3,\text{ref}}) .
\]

Here \( \Delta \phi_3 = \phi_{\text{oss}} - \phi_{\text{iss}} \) (V), is the potential difference between the ISS and the OSS, \( C_{\text{ox}} \) (mol/cm\(^3\)) is the concentration of electrons at the OSS for energy state \( j \), \( \Gamma_{\text{oss}} \) (mol/cm\(^3\)) is the total site concentration at the OSS for energy state \( j \) and in a manner analogous to that discussed above for the ISS, \( [\Gamma_{\text{iss}} - \Gamma_{\text{ss}}] \) (mol/cm\(^3\)) is the concentration of holes at the OSS for energy state \( j \). The total current across the semiconductor–electrolyte interface, \( I \) (A/cm\(^2\)), is the sum of all the individual interfacial currents, namely,

\[
I = \sum_{l=1}^{11} i_l .
\]
In the present work we will assume that the interface is operating under steady state conditions. In this event, at the IHP and the ISS, for individual species \( k \), the sum of the reaction rates, \( r_i \) (mol/cm\(^2\)s), over all of the reactions, \( l \), involving this species must be zero. In terms of Faradaic current \([7]\) \( i_{k,l} \) (A/cm\(^2\)), we may write

\[
\sum_{l} \frac{s_{k,l}}{nF} i_{k,l} = 0,
\]

where \( s_{k,l} \) is the stoichiometric coefficient for species \( k \) in reaction \( l \) and its sign depends on whether species \( k \) is a reactant or product in reaction \( l \).

At steady state, we apply Dirichlet boundary conditions to the concentrations of species \( k \) at the OHP and the OSS.

The potential difference across the interface, \( \Delta \phi = \phi_{\text{oxygen}} - \phi_{\text{hole}} \) (V), consists of the sum of the individual potential differences between the planes that constitute the double layer, namely,

\[
\Delta \phi = \Delta \phi_1 + \Delta \phi_2 + \Delta \phi_3,
\]

where \( \Delta \phi_1, \Delta \phi_2 \) and \( \Delta \phi_3 \) are as previously defined within the current equations given above. In the present work we assume that \( \Delta \phi \) is given. These individual potential differences are determined via the application of Gauss’ Law \([7]\) at the ISS and the IHP to yield,

\[
\frac{\epsilon_{sc}}{\delta_3} \Delta \phi_3 - \frac{\epsilon_2}{\delta_2} \Delta \phi_2 = F \sum_{i} \gamma_i e_n, \tag{25}
\]

and

\[
\frac{\epsilon_2}{\delta_2} \Delta \phi_2 - \frac{\epsilon_{soln}}{\delta_1} \Delta \phi_1 = F \sum_{i} \gamma_i t, \tag{26}
\]

respectively. Here \( \epsilon_{soln} \), \( \epsilon_2 \) and \( \epsilon_{sc} \) (F/cm) are the permittivities of the media between the OHP and IHP, between the IHP and ISS and between the ISS and OSS, respectively, \( \delta_1 \) and \( \delta_2 \) (cm) represent the of radii of the electrolyte species and \( \delta_3 \) is a measure of the distance from the surface of the semiconductor to the bulk such that electronic structure are that of the bulk.

Equations (22) to (26) represent our governing equations for the steady state dark current across the semiconductor–electrolyte interface of a DSC. The parameters that appear in these governing equations are the exchange current densities, \( i^{0}_{l,\text{ref}}, l = 1, 2, \ldots, 11 \), the corresponding reference measurements for concentrations, the reference equilibrium potentials for each reaction, \( \phi^{0}_{l,\text{ref}}, l = 1, 2, \ldots, 11 \), total site concentrations \( \Gamma_{\text{hp}}, \Gamma_{\text{ip}}, \Gamma_{\text{tp}}, \Gamma_{\text{cb}}, \Gamma_{\text{tc}}, \Gamma_{\text{val}} \), and \( \Gamma_{\text{ox}}, \phi_{\text{cb}}, \phi_{\text{tc}}, \phi_{\text{val}}, \phi_{\text{ox}} \), permittivities, \( \epsilon_{soln}, \epsilon_2, \) and \( \epsilon_{sc} \), and \( \delta_1, \delta_2 \), and \( \delta_3 \), and the boundary conditions for concentration of species \( \text{O}_x, \text{Red}_{\text{hp}}, \epsilon_{\text{cb}} \), and \( \epsilon_{\text{ox}} \) at the OHP and OSS.

For certain semiconductor–electrolyte combinations, such as gallium arsenide, some of these parameters have been identified. The measurement of the key interfacial kinetic parameters for the DSC system, however, is the focus of present experimental work by the authors. In lieu of these experimental values, in this initial work, we will consider a reduced interfacial model based on the model equations introduced above. Within the reduced model the number of unknowns is significantly decreased. Such a model may present itself as more industrially relevant in terms of the attainable kinetic parameters for the DSC system.

4 The Reduced Model

In an effort to retain some detail about the semiconductor surface and the loss mechanisms at the semiconductor–electrolyte interface, and to reduce the number of kinetic parameters required, we will now consider that the processes which give rise to the transfer currents between the OSS and ISS, and between the IHP and OHP, can be neglected. Thus the interfacial, steady state dark current described in this model is a result of electron and hole transfer between the electrolyte species and the CB, \( t \) and VB energy states of the semiconductor surface. These reactions are similar to those between the IHP and the ISS planes, as given in the complex interfacial model above and shown in Figure 2.

The interfacial dark current is now given by

\[
I = i_1 + i_2 + i_3, \tag{27}
\]

namely,

\[
I = i^{0}_{1,\text{ref}} \left( \gamma_{\text{cd}}^{b} \left[ \Gamma_{\text{cb}} \right]^{b} - \gamma_{\text{cb}}^{b} \right) n \lambda_1 (\Delta \phi - \phi^{0}_{1,\text{ref}}) - \frac{\gamma_{\text{cd}}^{a} \gamma_{\text{cd}}^{t}}{\gamma_{\text{cd}}^{a}} \lambda_2 (\Delta \phi - \phi^{0}_{1,\text{ref}}) + i^{0}_{2,\text{ref}} \left( \gamma_{\text{cd}}^{b} \left[ \Gamma_{\text{cb}} \right]^{b} - \gamma_{\text{cb}}^{b} \right) n \lambda_1 (\Delta \phi - \phi^{0}_{2,\text{ref}}) - \frac{\gamma_{\text{cd}}^{a} \gamma_{\text{cd}}^{t}}{\gamma_{\text{cd}}^{a}} \lambda_2 (\Delta \phi - \phi^{0}_{2,\text{ref}}) + i^{0}_{3,\text{ref}} \left( \gamma_{\text{cd}}^{b} \left[ \Gamma_{\text{cb}} \right]^{b} - \gamma_{\text{cb}}^{b} \right) n \lambda_1 (\Delta \phi - \phi^{0}_{3,\text{ref}}) - \frac{\gamma_{\text{cd}}^{a} \gamma_{\text{cd}}^{t}}{\gamma_{\text{cd}}^{a}} \lambda_2 (\Delta \phi - \phi^{0}_{3,\text{ref}}). \tag{28}
\]

Here the concentrations \( \gamma_{\text{cd}}, \gamma_{\text{cd}}^{b}, \gamma_{\text{cd}}^{t}, \gamma_{\text{cd}}^{a}, \) and \( \gamma_{\text{cd}}^{b} \) are assumed to be constant and given. The potential difference, \( \Delta \phi \), is the measured potential difference across the interface and is assumed to be given. In this reduced model the only parameters requiring experimental values are the exchange current densities \( i^{0}_{l,\text{ref}}, l = 1, 2, 3, \) and the corresponding reference concentrations, and reference potentials, and the total site concentrations at the ISS, \( \Gamma_{\text{cb}}, \Gamma_{\text{cb}}^{b}, \Gamma_{\text{cb}}^{a}, \) and \( \Gamma_{\text{cb}}^{t} \).

We also note that the form of our current is similar to the closed form interfacial current expressions given by Gerischer \([4]\), however we have additionally included the current produced (or consumed) by surface trap sites.
In lieu of the required experimental parameters, we analyse our interfacial current model by curve fitting to available experimental data and by looking at the behaviour of the free parameters. Assuming that concentrations of species at the IHP and the ISS are constant for all potential, $\Delta \phi$, the concentration ratios in front of the exponential terms in (28) must all be unity. Our free parameters for fitting are thus, $i_{1,ref}^0$, $i_{2,ref}^0$, $i_{3,ref}^0$, $\phi_{1,ref}^0$, $\phi_{2,ref}^0$, and $\phi_{3,ref}^0$. For our DSC system, TiO$_2$/I$_3^-/I^-$. we assume that the oxidation-reduction reaction is given by
\[ 3 \Gamma^- \frac{k_f}{k_b} I_3^- + 2 e^- , \] (29)
and hence $n = 2$ in expression (28). The remaining parameters are known constants and are assigned values of $F = 96485.3$ (C), $R = 8.31447$ (J/mol K) and $T = 298.15$ (K) [1].

We have used linear regression to fit (28) to experimental data, the results are shown in Figure 3. The experimental data was obtained from typical DSCs, however no dye was present on the surface of the TiO$_2$. Surface area of the DSC was approximately 1.5cm$^2$ and the electrolyte concentration was 0.2M I$_3^-$ and 0.6M I$^-$. The assumptions in our model that $n = 2$ and that concentrations at the ISS and IHP are constant for all potential values, limit the ability to obtain a reasonable curve fit. The fitted model curves are symmetrical sinh curves that do not exhibit the observed curvature at positive potential. In order to address this problem we need to examine the interfacial redox reaction assumed in (29).

There is a strong case for the adoption of a multistep redox reaction mechanism at the semiconductor–electrolyte interface in which the overall process is given by (29) [2, 10]. Examination of such a mechanism reveals that a value of $n = 1$ maybe more appropriate for our model. Fitting Equation (28) with $n = 1$ to our experimental data leads to only a slight improvement in the predicted curve (see Figure 3). A suitable fit can be obtained for a fractional value of $n$, however this would mean that some loss mechanism exists at the interface that has not been taken into account in our modelling, and presently we have no physical justification for this. However, given a multistep reaction sequence [2, 10], there may be surface blocking by electrolyte species, other than those involved in the direct reaction with the interface. In this case, we may be able to address the poor fit of our model by examining the scenario in which concentrations are not constant but rather functions of potential. This will result in current curves that are not symmetrical. This condition is presently under investigation by the authors.

6 Conclusions

We have presented the basic framework for a mathematical model of the current density across a semiconductor–electrolyte interface. The model accounts for many of the possible loss mechanisms and interactions between species at the interface. We have considered a reduced form of this interfacial model to investigate the TiO$_2$/I$_3^-/I^-$ semiconductor–electrolyte interface of a DSC. Validation of the model equations is on going in lieu of experimental results. Preliminary validation of the model against available experimental results, however, has indicated further investigation is required for the chemical reaction mechanism at the interface and for the functional form of the concentration parameters at the interface.

7 Acknowledgments

The authors wish to acknowledge the support of Sustainable Technologies International, Australia, and the Australian Research Council during the course of this research.

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