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Journal of Photochemistry and Photobiology A: Chemistry 164 (2004) 41–46

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Modelling interfacial charge transfer in dye-sensitised solar cells

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Received 25 July 2003; received in revised form 24 December 2003; accepted 24 December 2003

Abstract

A mathematical model of interfacial charge transfer within dye-sensitised solar cells (DSC) is presented for the semiconductor–dye–electrolyte interface. A general framework for the model equations of interfacial current is developed. The model accounts for the transfer of charge produced by reactions involving dye molecules, electrolyte species and adsorbed electrons at three semiconductor surface states. The model framework allows for identification of the required kinetic parameters necessary for solving the model equations. The general framework serves as a motivation for discussion on obtaining the required kinetic parameter values experimentally.

Keywords: Dye-sensitised solar cells; Electrode kinetics; Interfacial charge transfer

1. Introduction

The idea of sustainable and inexpensive energy has motivated interdisciplinary research into improving the dye-sensitised solar cell (DSC). The aspiration is to produce low-cost DSCs with a high enough efficiency to make them commercially viable. Mathematical modelling of the DSC will provide valuable insight into the cell for both researchers and industry. Such models can provide a time effective and accurate tool for identifying and investigating those mechanisms that are responsible for DSC operation and provide an avenue for insightful commentary on cell efficiency issues.

Understanding interfacial charge transfer at the semiconductor–dye–electrolyte interface within a DSC is important in identifying potential loss mechanisms. Modelling the transfer of charge at this interface will help identify possible approaches to improving the efficiency of the solar cell. However, realistic parameter values are required for the modelling work to have a physically realistic basis and be industrially relevant.

In this work, we present a mathematical model of the charge transfer at the semiconductor–dye–electrolyte interface in a DSC under steady-state, illuminated conditions that can be used to analyse the steady-state current produced at the interface. This is done by extending the work of Penny et al. [1] to include illuminated current. The motivation for presenting this model is to encourage discussion on obtaining the required kinetic parameters experimentally. These parameters are integral to the model equations describing interfacial charge transfer and once obtained, the model equations can be used to analyse loss mechanisms at the interface.

To date there have been a number of attempts to mathematically model the DSC. Ferber et al. [2], Ferber and Luther [3] and Stangl et al. [4], present simplified models of a complete DSC. The model by Ferber et al. [2] incorporates only one electron loss mechanism at the semiconductor–electrolyte interface, namely that from the TiO_2 conduction band to the redox couple in solution. Further recombination reactions involving the conduction band and surface trap states are ignored. The model equations at the interface represent modifications of the Boltzmann distribution [5] with one generation term for light induced reactions and one for the modelled electron loss. The characteristics of the dye were not modelled explicitly and the dependence of rate constants on energy potentials was not modelled for simplicity. In further work, Ferber and Luther [3] and Stangl et. al. [4] extend the Ferber et. al. [2] model to account for two spatial dimensions, however their approach to modelling the interface is the same.

Gerischer [6] 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

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doi:10.1016/j.jphotochem.2003.12.025

made concerning the concentrations of the redox couple in solution, the electrons and holes in the conduction band and in the valence band, and the electrons in the bulk of the semiconductor.

Orazem and Newman [7] 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 [5,6]), and includes many of the possible reactions involving the ionic species in the electrolyte and/or the electrons and holes in the semiconductor. 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 [8] 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.

Sodergen et al. [9] developed a steady-state theoretical model for the current–voltage (I–V) characteristics of microporous semiconductor films in photovoltaic cells. The model assumes that charge transfer in the bulk semiconductor occurs via diffusion and that the diffusion length of the electrons remain constant. No explicit model is given for charge transfer at the semiconductor–electrolyte interface.

Papageorgiou et al. [10] investigate electrolyte mass transport in thin layer nanocrystalline photoelectrochemical solar cells and do not model the complex behaviour of charge-transfer and charge-transport at the TiO_2–electrolyte interface. Instead, a constant effective electron injection rate is assumed throughout the cell and the study focuses on the mass transport of electrolyte species between and within the pores of the electrodes.

Matthews et al. [11] present a detailed model of the steady-state photocurrent produced by sensitised semiconductor electrodes. Many of the charge transfer reactions at the semiconductor–dye–electrolyte interface are considered, however the recombination reaction where excited dye molecules decay back to ground state was not considered, nor was the existence of surface states for adsorbed electrons at the interface.

2. Model development

In this section we propose the framework for a mathematical model of interfacial charge transfer within a DSC. We firstly consider the reactions constituting the dark current and their corresponding current density equations as presented in Penny et al. [1]. We then extend this work to include the photon mediated reactions representing the illuminated current.

2.1. Previous work: the non-illuminated interfacial current

The reduced interfacial model for non-illuminated current, detailed in Penny et al. [1], considers the charge transfer between electrolyte species and surface states for adsorbed electrons on the surface of the semiconductor. The surface of the semiconductor is considered to consist of three surface states of discrete energy levels, those corresponding to the conduction band (*cb*) and valance band (*vb*) of the semiconductor and an intermediate energy level surface state, denoted as trap (*t*). The physical interpretation of *t* sites is given by noting that at the surface there are flaws in the crystal causing dangling bonds in the lattice creating trap sites for electrons. Trap sites may also be created by impurities adsorbed on the surface of the semiconductor. These sites usually have energy levels between the *cb* and the *vb* [12]. The electrolyte solution is assumed to be binary, consisting of an oxidant (Ox) and reductant (Red) and a solvent. The structure of the semiconductor–electrolyte interface and the non-illuminated reactions are shown schematically in Fig. 1.

In their work, Penny et al. [1] consider three non-illuminated reactions that occur between the semiconductor surface and the electrolyte species. The oxidation and reduction of ionic species in the electrolyte occurs via reactions $1, 2$ and 3 shown in Fig. 1. The forward direction chosen for each of these reactions is the movement of electrons into or towards the semiconductor, and furthermore, each of these reactions is assumed to be reversible. An example of these reactions, in the forward direction, is reaction 1 where an adsorbed reductant species donates an electron, or electrons, into the *cb* energy state and is itself oxidised. The three electrochemical reactions depicted in Fig. 1 are reversible and are represented by the general expression,

$$b\text{Red} + nh^i \underset{k_{\mathrm{b},l}}{\overset{k_{\mathrm{f},l}}{\rightleftharpoons}} a\text{Ox} + ne^i. \tag{1}$$

Here e represents electrons, h represents vacant sites, or holes, at the semiconductor surface, and a, b, and n are stoichiometric coefficients. The subscript l designates the particular reaction under investigation so that $k_{\mathrm{f},l}$ and $k_{\mathrm{b},l}$

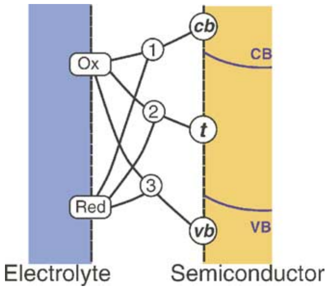

Fig. 1. Identified non-illuminated current reactions at the semiconductor–dye–electrolyte interface.

are the rate constants for the forward and backward reactions of reaction l, respectively. The value of l in expression (1) will be either $1, 2$ or 3, where these labels coincide with those used to label the reactions in Fig. 1. The superscript i in the expression (1) designates the energy state which acts as the source of the electrons and holes at the surface of the semiconductor, e and h, respectively, for a particular reaction. Thus when $l = 1$, $i = cb$; when $l = 2$, $i = t$; and when $l = 3$, $i = vb$.

The current density, i_l (A/cm^2), associated with the semiconductor–electrolyte charge transfer reaction l described in (1), is given by the forward current density minus the backward current density, namely [12],

$$i_l = nF(k^0_{\mathrm{f},l}[\mathrm{Red}]^b[h^i]^n \exp[(1-\beta)nf\Delta\phi] - k^0_{\mathrm{b},l}[\mathrm{Ox}]^a[e^i]^n \exp[-\beta nf\Delta\phi]). \quad (2)$$

Here [ ] (mol/cm^2) denotes concentration, $\Delta\phi = \phi_{\mathrm{sc}} - \phi_{\mathrm{soln}}$ (V), is the potential difference between the semiconductor and the solution, F (C/mol) is Faraday's constant, β the transfer coefficient usually taken as one half and $f = F/RT$, where R (J/K mol) is the molar gas constant and T (K) the temperature. Furthermore, $k^0_{\mathrm{f},l}$ and $k^0_{\mathrm{b},l}$ are the pre-exponential components of the Arrhenius relationship [5] for the forward and backward rate constants.

Using the current expression in (2) the equilibrium potential for reaction l, ϕ^0_l (V), may be expressed as a function of species concentrations and rate constants, namely [1],

$$\phi^0_l = -\frac{1}{nf}\left[\ln\frac{k^0_{\mathrm{f},l}}{k^0_{\mathrm{b},l}} + \ln\frac{[\mathrm{Red}]^b[h^i]^n}{[\mathrm{Ox}]^a[e^i]^n}\right]. \quad (3)$$

At a given reference state (3) becomes [1],

$$\phi^0_{l,\mathrm{ref}} = -\frac{1}{nf}\left[\ln\frac{k^0_{\mathrm{f},l}}{k^0_{\mathrm{b},l}} + \ln\frac{[\mathrm{Red}_{\mathrm{ref}}]^b[h^i_{\mathrm{ref}}]^n}{[\mathrm{Ox}_{\mathrm{ref}}]^a[e^i_{\mathrm{ref}}]^n}\right], \quad (4)$$

were the subscript ref denotes values measured at the chosen reference state.

At equilibrium the forward current density for reaction l is equal to the corresponding backward current density and the exchange current density i^0_l (A/cm^2), can be defined as the value of these currents. This exchange current density is given by [1],

$$i^0_l = nFk^0_{\mathrm{f},l}[\mathrm{Red}]^b[h^i]^n \exp[(1-\beta)nf\phi^0_l] = nFk^0_{\mathrm{b},l}[\mathrm{Ox}]^a[e^i]^n \exp[-\beta nf\phi^0_l]. \quad (5)$$

Combining (3) and (5) the general expression for i^0_l is obtained, namely [1],

$$i^0_l = nF(k^0_{\mathrm{f},l}[\mathrm{Red}]^b[h^i]^n)^\beta(k^0_{\mathrm{b},l}[\mathrm{Ox}]^a[e^i]^n)^{(1-\beta)}. \quad (6)$$

Now combining (2)–(4) and (6) an expression for the transfer current densities, written with respect to reference conditions, generated by the reactions between surface states on the semiconductor and adsorbed electrolyte species is obtained, namely [1],

$$i_l = i^0_{l,\mathrm{ref}}\left(\frac{[\mathrm{Red}]^b[\Gamma^i - e^i]^n}{[\mathrm{Red}_{\mathrm{ref}}]^b[\Gamma^i - e^i_{\mathrm{ref}}]^n} \times \exp\left[(1-\beta)nf(\Delta\phi - \phi^0_{l,\mathrm{ref}})\right] - \frac{[\mathrm{Ox}]^a[e^i]^n}{[\mathrm{Ox}_{\mathrm{ref}}]^a[e^i_{\mathrm{ref}}]^n} \times \exp\left[-\beta nf(\Delta\phi - \phi^0_{l,\mathrm{ref}})\right]\right). \quad (7)$$

Here $\phi^0_{l,\mathrm{ref}}$ is the reference potential for reaction l, e^i (mol/cm^2) the concentration of electrons at the surface energy state i and Γ^i (mol/cm^2) the total site concentration for energy state i. Furthermore, assuming that the only species present on the surface of the semiconductor are e and h and that a hole is formed by the absence of an electron, then $[\Gamma^i - e^i]$ (mol/cm^2) represents the concentration of holes at the surface energy state i. In addition, in equation (7), $i^0_{l,\mathrm{ref}}$ (A/cm^2) is the reference exchange current density for reaction l and is given by [1],

$$i^0_{l,\mathrm{ref}} = nF\left(k^0_{\mathrm{f},l}[\mathrm{Red}_{\mathrm{ref}}]^b[h^i_{\mathrm{ref}}]^n\right)^\beta \times \left(k^0_{\mathrm{b},l}[\mathrm{Ox}_{\mathrm{ref}}]^a[e^i_{\mathrm{ref}}]^n\right)^{(1-\beta)}. \quad (8)$$

The required kinetic parameters for these oxidation/reduction reactions are the reference exchange current densities for each reaction l, $i^0_{l,\mathrm{ref}}$, the corresponding reference potentials, $\phi^0_{l,\mathrm{ref}}$, and the corresponding reference concentrations $[\mathrm{Ox}_{\mathrm{ref}}]$, $[\mathrm{Red}_{\mathrm{ref}}]$, $[e^i_{\mathrm{ref}}]$ and the total site concentrations Γ^i for each energy state i.

2.2. Illuminated interfacial current

Here we extend the model of Penny et al. [1] to account for the illuminated current at the semiconductor–dye–electrolyte interface within a DSC. The presented model framework identifies the required kinetic parameter values to enable the interfacial current within the DSC to be mathematically modelled and analysed.

On the scale of a porous DSC cathode, we assume that the semiconductor–dye–electrolyte interface has no appreciable length and that such interfaces exist as planes within the electrode assembly. On the scale of the interface itself, we assume the existence of three planes, between which the spatial gradient of concentration and potential is negligible. These planes represent the adsorbed electrolyte species, the adsorbed electrons on the surface of the semiconductor and the dye layer. This assumed structure, along with the identified photon mediated interfacial charge transfer reactions, are shown schematically in Fig. 2. These reactions occur either between the dye molecules and adsorbed electrons at the semiconductor surface or between the dye molecules and the adsorbed electrolyte species. As with the dark current

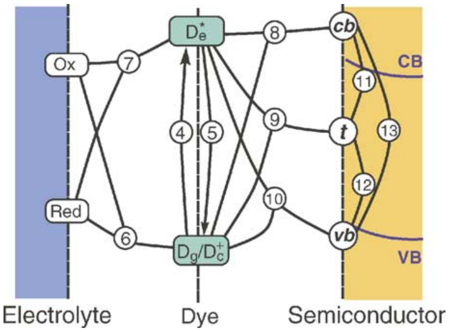

Fig. 2. Identified illuminated current reactions at the semiconductor–dye–electrolyte interface.

model given in Section 2.1, the forward direction of a reaction has been chosen as the movement of electrons into or towards the semiconductor.

Reactions 4 and 5 are associated with photon absorption by a ground state dye molecules D_g and do not explicitly contribute to the total interfacial current. However, these reactions do effect the concentrations of the dye molecules which in turn effect the currents produced by other interfacial reactions involving dye molecules. Reaction 4 represents the absorption of a photon by D_g resulting in an excited dye molecule, D_e^*, and reaction 5 represents the decay of D_e^* back to D_g without the release of an electron. These reactions are non-reversible and are given by the expressions

$$D_g + \text{photon}_{\text{abs}} \overset{k_{f,4}}{\rightarrow} D_e^*, \qquad (9)$$

and

$$D_e^* \overset{k_{f,5}}{\rightarrow} D_c^+, \qquad (10)$$

respectively. Here photon$_{\text{abs}}$ represents only photons that are absorbed by the ground state dye molecule. The forward rates of reactions, r_l (mol/cm^{2}s), for the reactions given by expressions (9) and (10), are

$$r_4 = k_{f,4}[D_g][\text{photon}_{\text{abs}}], \qquad (11)$$

and

$$r_5 = k_{f,5}[D_e^*], \qquad (12)$$

respectively. We have assumed here that the forward rate constants $k_{f,4}$ and $k_{f,5}$ are unaffected by potential.

The oxidation and reduction reactions between dye molecules and electrolyte species are given by reactions 6 and 7 in Fig. 2. The reduction of an oxidant species in the electrolyte by an excited dye molecule, denoted as reaction 6 in Fig. 2, is represented by the chemical equation,

$$b\text{Red} + nD_c^+ \underset{k_{b,6}}{\longrightarrow} a\text{Ox} + nD_e^*, \qquad (13)$$

where D_c^+ represents the cationic dye molecule. This reaction is not reversible and is a loss mechanism at the interface. As such, the current produced by this reaction is opposite in sense to our chosen forward direction; that of electrons moving towards or into the semiconductor. The rate for the reaction represented by Eq. (13) is,

$$r_6 = -k_{b,6}^0[\text{Ox}]^a[D_e^*]^n \exp[-\beta nf\Delta\phi_1], \qquad (14)$$

where $\Delta\phi_1 = \phi_{\text{dye}} - \phi_{\text{soln}}$ is the potential difference between the dye layer and the plane of adsorbed electrolyte species.

Reaction 7 in Fig. 2 represents the reduction of D_c^+, by the reductant species in the electrolyte, to form D_g. This non-reversible reaction is represented by,

$$b\text{Red} \; + nD_c^+ \overset{k_{f,7}}{\rightarrow} \; a\text{Ox} + nD_g. \qquad (15)$$

The forward rate for the reaction described by expression (15) is,

$$r_7 = k_{f,7}^0[\text{Red}]^b[D_c^+]^n \exp[(1-\beta)nf\Delta\phi_1]. \qquad (16)$$

The injection of electrons into the semiconductor from excited dye molecules is represented by reactions 8, 9 and 10 in Fig. 2. The forward direction for each of these reactions involves an excited dye molecule donating an electron into a surface state of the semiconductor. This is represented by the expression,

$$D_e^* + h^i \; \rightarrow^{k_{f,l}} \; D_g^+ + e^i, \qquad (17)$$

where the subscript l denotes the particular reaction under investigation. The value of l in expression (17) will be either 8, 9 or 10, where these labels coincide with those used to label the reactions in Fig. 2. The superscript i in the expression (17) designates the energy state which is accepting the donated electron. Thus when $l = 8$, $i = cb$; when $l = 9$, $i = t$; and when $l = 10$, $i = vb$. The forward rate of reaction l, $r_{f,l}$ (mol/cm^2 s), is then given by,

$$r_{f,l} = k_{f,l}^0[D_c^+][\Gamma^i - e^i] \exp[(1-\beta)nf\Delta\phi_2], \qquad (18)$$

where $\Delta\phi_2 = \phi_{\text{sc}} - \phi_{\text{dye}}$ is the potential difference between the semiconductor surface states and the dye layer. The backward direction of reactions 8, 9 and 10 in Fig. 2 correspond to the loss of electrons from the surface states of the semiconductor causing the reduction of the cationic dye molecule, D_c^+, to the ground state, D_g. This is represented by the expression,

$$D_g + h^i \; \underset{k_{b,l}}{\leftarrow} \; D_c^+ + e^i. \qquad (19)$$

The backward rate of reaction l, $r_{b,l}$ (mol/cm^{2}s), is then given by,

$$r_{b,l} = -k_{b,l}^0[D_c^+][e^i] \exp[-\beta nf\Delta\phi_2]. \qquad (20)$$

In this work, we assume that adsorbed electrons can move between semiconductor surface states due to thermal agitation and photon absorption. These reactions are shown in Fig. 2 as reactions 11, 12 and 13 and they do not contribute to the total interfacial current. However, these reactions do effect the concentrations of adsorbed electrons. The general chemical reaction associated with the movement of electrons on the surface of the semiconductor is given by,

$$e^i + h^j + \text{photon} \underset{k_{\mathrm{b},l}}{\overset{k_{\mathrm{f},l}}{\rightleftharpoons}} h^i + e^j, \tag{21}$$

where again the subscript l denotes the particular reaction under investigation. The value of l in expression (21) will be either 11, 12 or 13, where these labels coincide with those used to label the reactions in Fig. 2. The superscript i in the expression (21) designates the energy state which acts as the source of the electron for the forward direction and superscript j designates the acceptor energy state (holes) for the electron in the forward direction. Thus when $l = 11$, $i = t$ and $j = cb$; when $l = 12$, $i = vb$ and $j = t$; and when $l = 13$, $i = vb$ and $j = cb$. The rate, r_l (mol/cm^{2}s), of reaction l is then given by,

$$r_l = k_{\mathrm{f},l}[e^i][\Gamma^j - e^j][\text{photon}] - k_{\mathrm{b},l}[\Gamma^i - e^i][e^j]. \tag{22}$$

2.3. System of model equations and the required kinetic parameters

The total current across the semiconductor–dye–electrolyte interface, I (A/cm^2), is the sum of the currents of the individual interfacial reactions that contribute to the total current across the interface, namely,

$$I = \sum_{l=1}^{3} i_l + F\sum_{l=8}^{10} n_l r_l, \tag{23}$$

where n_l represents the number of electrons transferred in reaction l.

In order to obtain the total interfacial current I in expression (23), boundary conditions on the steady-state concentrations of adsorbed electrolyte species, Ox and Red, and adsorbed electrons on the surface of the semiconductor at energy state i, e^i, needs to be specified. In practice these concentrations will be affected by the mass transport processes that occur within the bulk of the electrolyte solution and the bulk of the semiconductor.

In the absence of models for the bulk electrolyte and semiconductor one can assume constant and known concentrations of species at the semiconductor surface states and the electrolyte species. Such an assumption about the boundary data may be motivated via a specific cell configuration and/or specific cell operating conditions. For example, the discharge of an extremely thin DSC cathode in well stirred, excess electrolyte solution under short circuit conditions. We note, however, that if one assumes known concentrations of adsorbed electrons at semiconductor surface states then the reactions 11, 12 and 13, shown in Fig. 2, are not necessary for the system of model equations.

The concentration of the dye molecules, $\mathrm{D_g}$, $\mathrm{D_e^*}$ and $\mathrm{D_c^+}$, at the dye layer is governed by the reactions that involve each dye species.

Assuming that the interface is operating under steady-state conditions then for each individual dye species, k, the sum of the reaction rates, r_l (mol/cm^2 s), over all of the reactions, l, involving this species must be zero. In terms of reaction rates $r_{k,l}$ (mol/cm^{2}s), we may write,

$$\sum_l s_{k,l} r_{k,l} = 0, \tag{24}$$

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

The potential difference across the interface, $\Delta\phi = \phi_{\mathrm{sc}} - \phi_{\mathrm{soln}}$ (V), consists of the sum of the two interfacial potential differences $\Delta\phi_1$ and $\Delta\phi_2$, namely,

$$\Delta\phi = \Delta\phi_1 + \Delta\phi_2, \tag{25}$$

where $\Delta\phi_1 = \phi_{\mathrm{dye}} - \phi_{\mathrm{soln}}$ and $\Delta\phi_2 = \phi_{\mathrm{sc}} - \phi_{\mathrm{dye}}$, as previously defined within the rate equations given above. Assuming that $\Delta\phi$ is known then the individual potential differences can be determined via the application of Gauss' Law [12] at the dye layer to yield,

$$\frac{\epsilon_{\mathrm{sc}}}{\delta_{\mathrm{sc}}}\Delta\phi_2 - \frac{\epsilon_{\mathrm{soln}}}{\delta_{\mathrm{soln}}}\Delta\phi_1 = F[\mathrm{D_c^+}]. \tag{26}$$

Here ϵ_{soln} and ϵ_{sc} (F/cm) are the permittivities of the media between the dye layer and solution, and between the dye layer and semiconductor, respectively, δ_{soln} (cm) represents the sum of the radii of the electrolyte species and the radii of the de molecule and δ_{sc} is a measure of the radii of the dye molecules.

Eqs. (23)–(26) represent our governing equations for the steady-state current across the semiconductor–dye–electrolyte interface of a DSC. The parameters that appear in these governing equations are the exchange current densities, $i^0_{l,\mathrm{ref}}$ (for $l = 1, 2, 3$), the corresponding reference measurements for concentrations and equilibrium potentials, $\mathrm{Red_{ref}}$, $\mathrm{Ox_{ref}}$, e^i_{ref} and $\phi^0_{l,\mathrm{ref}}$, respectively, rate constants $k^0_{\mathrm{f},l}$ and $k^0_{\mathrm{b},l}$, surface site concentrations Γ^{cb}, Γ^t, and Γ^{vb}, permittivities, ϵ_{soln} and ϵ_{sc}, radii measurements δ_{soln} and δ_{sc}, and the boundary conditions for the concentration of species Ox, Red, e^{cb}, e^t and e^{vb}.

3. Discussion and conclusions

We have presented the framework for a mathematical model of the current produced at the semiconductor–dye–electrolyte interface in a DSC under illuminated and non-illuminated conditions. The general model accounts for the transfer of charge produced by reactions involving dye molecules, electrolyte species and adsorbed electrons at three semiconductor surface states, namely, the valance band, the conduction band and trap states. The model framework has allowed identification of the required kinetic parameters, such as exchange current densities and rate constants, that are necessary for solving the model equations. It is hoped that this general framework will serve as a motivation for discussion on obtaining the required kinetic parameter values experimentally. The establishment of such parameter values will allow the model to be utilised effectively and facilitate the analysis of loss mechanisms associated with the interfacial current within a DSC.

The model equations presented for non-illuminated current, based on the model from Penny et al. [1], are written with respect to reference exchange current densities. This reference state eliminates the need for forward and backward rate constants for reactions 1, 2 and 3 in Fig. 1. However, this introduces the need for reference potentials and concentration values. An obvious choice for a reference state is the equilibrium state of each reaction, the state in which there is no net current produced by the reactions constituting the dark current. The model for non-illuminated current presented in Penny et al. [1] was validated by fitting the proposed model to available experimental data. This fit enabled examination of the validity of the model in lieu of the required parameter values for dark current. The results indicated that there was a strong case for the adoption of a multistep redox reaction mechanism at the semiconductor–electrolyte interface. The results also indicated that the concentration of redox species at the interface and adsorbed electrons are not constant but rather functions of potential. This condition is presently under investigation by the authors through the development of models for the bulk semiconductor and electrolyte.

The illuminated current produced at the semiconductor–dye–electrolyte interface was modelled here by extending the non-illuminated model in Penny et al. [1]. The detailed framework presented identifies charge transfer reactions at the semiconductor–dye–electrolyte interface and explicitly lists the required kinetic parameters. If such a model framework was to be adopted in its entirety then one is left with a large number of kinetic parameter values to be obtained. Investigation into obtaining these values is a necessary process in order to gain the benefits that this model may allow for analysis of interfacial charge transfer loss mechanisms. Clearly the identification of those parameters that can be measured and those that are unattainable will enable the model to be adapted to be more industrially and physically relevant.

Adaption of the model framework presented here in a way that consistently accounts for the few kinetic parameter values available in the literature is currently being undertaken by the authors.

Acknowledgements

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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