Available online at www.sciencedirect.com

ScienceDirect

Solar Energy Materials & Solar Cells 92 (2008) 11–23

Solar Energy Materials and Solar Cells

www.elsevier.com/locate/solmat

A mathematical model for interfacial charge transfer at the semiconductor–dye–electrolyte interface of a dye-sensitised solar cell

Melissa Penny[a], Troy Farrell[a,*], Colin Please[b]

[a]School of Mathematical Sciences, Queensland University of Technology, Brisbane, Qld. 4001, Australia
[b]School of Mathematics, University of Southampton, Southampton SO17 1BJ, UK

Received 19 January 2007; received in revised form 27 July 2007; accepted 31 July 2007
Available online 27 September 2007

Abstract

A mathematical model for the interfacial charge transfer within dye-sensitised solar cells (DSC) is presented for the semiconductor–dye–electrolyte interface. The model explicitly accounts for each reaction at the interface involving dye molecules, electrolyte species and adsorbed electrons associated with the conduction band surface states of the semiconductor. Additionally, the model accounts for photoelectron injection via singlet and triplet excited dye states. The governing equations can be used to describe the total current produced by the DSC under illuminated and non-illuminated conditions, at steady state. Regular perturbation methods are applied to the model equations to obtain closed form analytic approximations, resulting in approximate solutions that negate the need for numerical solution of the model system. All parameter values associated with the model are obtained from the literature and from experimental data. The presented numerical results and analytic approximations compare favourably to experimental data, capturing the interfacial characteristics of current versus voltage curves of the DSC.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Dye-sensitised solar cells; Interfacial charge transfer; Mathematical modelling

1. Introduction

The need for credible and reliable renewable energy is widely recognised across the globe. Photoelectrochemical cells, such as dye-sensitised solar cells (DSCs), provide an alternative to present day p–n junction photovoltaics. The DSC, shown in Fig. 1, is constructed by depositing semiconductor particles, such as TiO_2, onto a glass plate which is coated with a layer of a transparent conductive oxide (TCO), for example, tin oxide (SnO_2). This transparent conducting electrode (TCE) is the current collector electrode of the solar cell. The anatase TiO_2 particles are approximately 10–25 nm in diameter [1] and are sintered together to form a nanoporous film of approximately 10 μm in width with a porosity of approximately 50–65% [2,3]. The porous film has a large internal surface area and is coated with a monolayer layer of light absorbing dye capable of charge transfer. An example of such a dye is the ruthenium (Ru) dye complex, the N3 Ru dye, namely $cis-\mathrm{Ru(SCN)_2L_2}$ ($\mathrm{L} = 2,2'$-bipyridyl-4, 4′-dicarboxylate). We refer to the dyed nanoporous film as the DSC anode; this film constitutes the DSC working electrode. The dye coated TiO_2 electrode is flooded with the electrolyte system consisting of a redox couple in solution, for example, iodide (I^-) and triiodide (I_3^-). The counter electrode is formed by sandwiching the semiconductor–dye–electrolyte between the existing TCE and another TCO coated glass plate. The counter electrode adjacent to the electrolyte is covered with platinum, which acts as a catalyst for the redox reaction between the electrolyte and the TCO.

During operation, the solar cell is illuminated through the electrode contacting the semiconductor, the current collector, as shown in Fig. 1. Upon illumination of the cell, adsorbed dye molecules at ground state, D_g, absorb photons of an appropriate wavelength and are excited to a new state, D_{e1}^*. The excited molecules inject electrons, at a high rate (ultrafast injection), into the conduction band of the TiO_2 semiconductor, and the molecules of dye are

---

*Corresponding author. Tel.: +61 7 3138 2364; fax: +61 7 3138 2310.
E-mail address: t.farrell@qut.edu.au (T. Farrell).

0927-0248/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2007.07.013

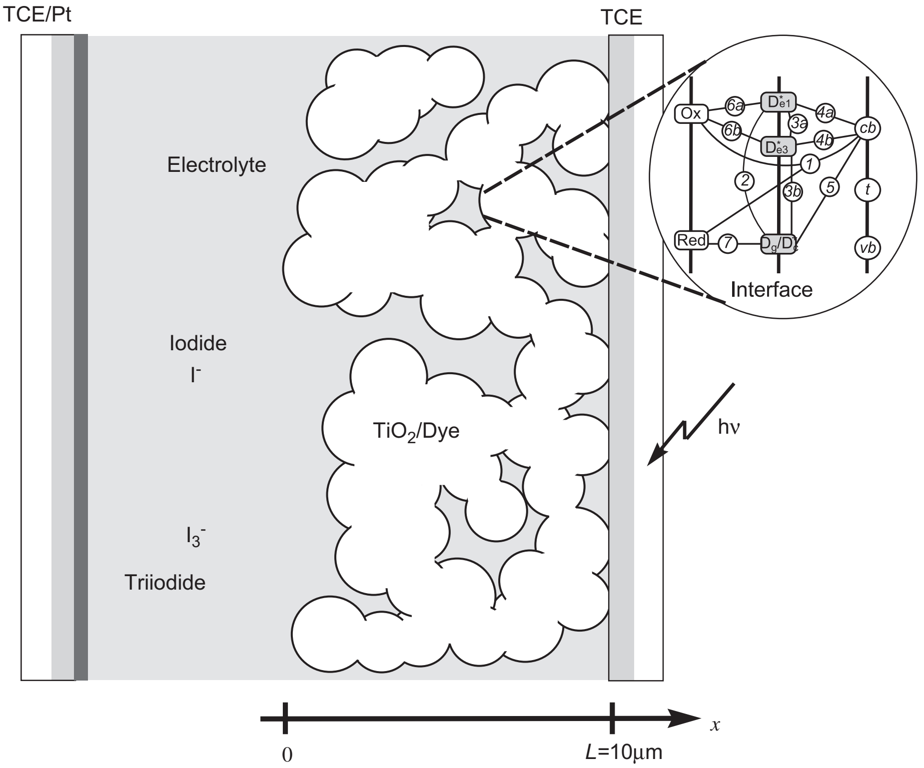

Fig. 1. Schematic diagram of the DSC illustrating the length of the anode and the semiconductor–dye–electrolyte interface.

oxidised to cations, D_c^+. The electrons in the TiO_2 diffuse through the solid to the glass electrode and out of the cell, yielding useable energy. These electrons enter the counter electrode where they reduce the oxidant I_3^- to I^-. The I^- ions are transported through the electrolyte solution and eventually contact the oxidised dye molecules. The I^- ions are then oxidised in a reaction that returns the oxidised dye molecules to their ground state.

DSCs are comparatively inexpensive to manufacture, and provide clean and inexpensive power. Presently, DSCs operate at between 7 and 11% efficiency [4]. To compete against conventional photovoltaics on the commercial market, DSCs require increased efficiency, increased stability and lower manufacturing costs. Mathematical modelling of DSCs may provide valuable insight into the cell, allowing researchers to identify loss mechanisms and to suggest improvements for overall cell efficiency.

To date there have been numerous mathematical and electrical models of the DSC that have been developed. Here we consider how these models describe the semiconductor–dye–electrolyte interface. Ferber et al. [5] present a model of a complete DSC and consider only one interfacial loss mechanism: relaxation from the TiO_2 conduction band to the redox electrolyte. Generation of electrons via the injection from excited dye molecules is accounted for using Beer–Lambert's law [6], and the ratio of rates of reactions involving these electrons give a modified Boltzmann's approximation [7] for the electron density. The characteristics of the dye were not modelled explicitly and the dependence of rate constants on energy potentials were not modelled for simplicity. In further work, Ferber and Luther [8] extend the Ferber et al. [5] model to account for two spatial dimensions, however, their approach to modelling the interface is the same.

Other models of the DSC, or other solar cells, that consider the semiconductor–dye–electrolyte, or semiconductor–electrolyte, interface include Soedergren et al. [9] and Cao et al. [10]. Soedergren et al. [9] develop a steady-state theoretical model and provide no explicit model of the semiconductor–electrolyte interface. Cao et al. [10] extend the work of Ref. [9] to a model of a DSC that includes the transient response of the cell. The model does not take into account all the complex processes involved with charge transfer in the semiconductor, but instead includes only a Beer–Lambert's law to account for the production of electrons under illumination and a simplified loss term that is dependent on the electron concentration and lifetime. Beer–Lambert's law is also utilised by Papageorgiou et al. [11] and Peter and Wijayantha [12] to describe the electron production. Papageorgiou et al. [11] also describe the interfacial oxidation–reduction reaction via a Butler Volmer expression and in Peter and Wijayantha [12] the loss of electrons is described by the ratio of electron concentration to electron lifetime. In both works each interfacial reaction at the semiconductor–dye–electrolyte interface is not modelled explicitly. Peter et al. [13] also utilise a model similar to Peter and Wijayantha [12] but additionally include reactions of electrons with oxidised dye molecules, and of dye molecules with the electrolyte species.

Download English Version:

https://daneshyari.com/en/article/80181

Download Persian Version:

https://daneshyari.com/article/80181

Daneshyari.com