Transient Photocurrents in Dye-Sensitized Nanocrystalline Solar Cells

Alison B. Walker*[a], L. M. Peter[b], D. Martínez[a], and K. Lobato[b]

Abstract: The time varying photocurrent response of dye-sensitized solar cells to switching on illumination and then switching the illumination off after steady state has been reached has been measured and modeled with a multi-scale Monte Carlo and continuum approaches within the multiple trapping picture, where electrons in the porous TiO_2 electrodes undergo successive trapping and detrapping events. These models are more detailed than the more common formalism employing an effective diffusion coefficient as they take into account the large variation in conduction electron density with distance and time near the extracting electrodes. Agreement between the three sets of results using a trap concentration and trap energy distribution width from a separate set of measurements using charge extraction shows that the multiple trapping formalism holds.

Keywords: Dye-sensitized cell · Electron transport · Monte Carlo · TiO_2 · Traps

Introduction

Dye-sensitised cells are promising as low-cost solar cells that could be used as power-producing windows or skylights.[1] Cell operation is shown in Fig 1. Light absorption occurs in dye molecules adsorbed on a highly porous structure of sintered nanoparticles of TiO_2. Dye excitation is followed by electron injection into the TiO_2 and regeneration *via* a redox electrolyte containing iodide (I^-) and triiodide (I_3^-) ions. Electrons are transported through the TiO_2 nano-particles to the front contact, which consists of a transparent conductive oxide layer. The
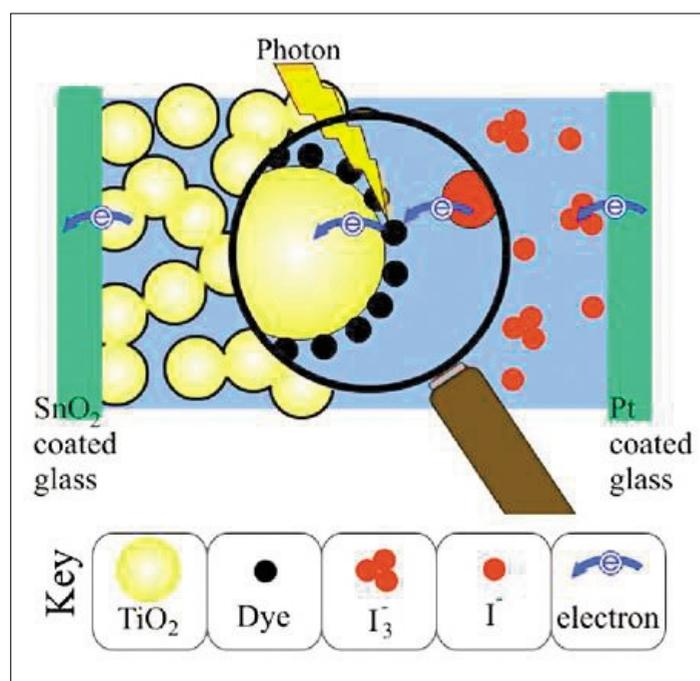

Fig. 1. Schematic diagram illustrating operation of the dye-sensitized cell

Correspondence: Dr. A. B. Walker[a]
[a]Department of Physics,
University of Bath,
Bath BA2 7AY, UK
University of Bath
Tel.: +44 1225 383 322
Fax: +44 1225 386 110
E-Mail: A.B.Walker@bath.ac.uk
[b]Department of Chemistry

contact to the redox electrolyte is made by a catalyst-coated back contact.

Much effort has gone into their characterization and modeling.[2] Electron transport through the TiO_2 film continues to be the subject of intense debate since the photocurrent response is surprisingly slow, with risetimes ranging from milliseconds to seconds depending on light intensity. Most data on electron transport has been interpreted within the multiple trapping

(MT) model,[3] where the motion of photoinjected electrons through a well defined conduction band with minimum energy E_C is interrupted by a series of trapping and detrapping events. A large concentration of trap states exists within the TiO_2 film[4] and these traps are filled under illumination up to $_nE_F$ where $_nE_F$ is the quasiFermi level energy. The position of $_nE_F$ relative to the redox level $E_{F,redox}$ is determined by the conduction electron density n_c in terms

of the thermal energy $k_B T$ where k_B is the Boltzmann constant and T the absolute temperature by

$$_n E_F - E_{F,redox} = k_B T \ln\left(\frac{n_c}{n_{eq}}\right) \qquad (1)$$

where n_{eq} is the value of n_c when $_n E_F = E_{F,redox}$ *i.e.* in the dark. Thus the traps fill as the illumination intensity increases. The detrapping time τ_d from a trap of energy E_T depends exponentially on how far the trap level is below the conduction band so the further $_n E_F$ is from the conduction band, the longer the electrons take to detrap and the slower the transport. Thus τ_d is a sensitive function of n_c.

Kopidakis *et al.*[5] have used data on effective electron diffusion coefficients D_{eff} deduced from measured photocurrent transients to argue that the MT model cannot be used to interpret transient response. They obtain their values of D_{eff} from $D_{eff} = L^2/\tau$ where τ is the time to collect half the photoinjected charge and the distance traveled by the electrons L is half the film thickness d. This method for calculating D_{eff} assumes that τ is similar for all electrons. However, within the MT picture, τ is dominated by τ_d. Since n_c and thus $_n E_f$ decrease strongly with time as the charge empties out of the cell and also vary sharply at the extracting electrode, τ and D_{eff} are poorly defined quantities.

Here, we take a related approach to Kopidakis *et al.*[5] by making transient measurements of the photocurrent for a large amplitude illumination pulse, but, in this case, the pulse lasts seconds so that steady state is achieved during the pulse. We interpret the transient photocurrents with two models of electron transport based on the MT model, a multiscale random walk Monte Carlo model[6,7] and a continuum model.[8] Both models employ the diffusion coefficient D_0 of conduction electrons without traps, by explicitly considering trapped electrons. They allow for the sharp distance and time variation in $_n E_F$ at the extracting contact noted above. Experimental data from the charge extraction technique[3] has shown that the trap energy distributions are of the form

$$g(E_T) = \left(\frac{N_{t,0}}{k_B T_c}\right) \exp\left[-\frac{E_c - E_T}{k_B T_c}\right] \qquad (2)$$

where T_c is a characteristic temperature defining the width of the trap distribution, such that the smaller T_c is, the greater the likelihood of shallow traps. In our models we have obtained good agreement with experimental data using values of $N_{t,0}$ and T_c from the literature[4], thus we argue that this comparison vindicates the MT model.

Experiment

The FTO glass substrate (TEC 15 Pilkington USA) was cleaned before the application of a blocking layer as described elsewhere.[2] The TiO_2 colloid was spread by doctor blading using a circular Scotch tape mask to give a 5 mm diameter disk (0.196 cm^2). After drying in air, the TiO_2 was sintered in air at 450 °C for 25 min using a hot air gun to give porous anatase films about 5 μm thick measured using a Dektak 6 M profilometer. The TiO_2 particle sizes are specified by the supplier to be 9 nm diameter.

To reduce the series resistance of the finished cell, a layer of gold buffered by chromium was added to the working and counter electrodes by thermal vacuum evaporation. A 7 mm diameter disk was used to mask out the areas where the TiO_2 and electrolyte would contact. This had the effect of reducing the geometric series resistance of the cells from 25 Ω to 5 Ω. The films were sensitized with N719. Before being added to the sensitizing solution they were heated to 80 °C to prevent water and other organics from adsorbing. The semi-transparent FTO counter electrode was platinised by sputter coating and heat treated at 200 °C for 15 min to remove organic impurities from sputter coating and thus make the platinum film more stable. The working and counter electrodes were held together by a 20 μm hotmelt spacer. The electrolyte was introduced *via* a small hole in the counter electrode and consisted of 0.1M Li and 0.05M LiI in acetonitrile containing 0.5 tertiary butyl pyridine.

Under AM1.5 simulated solar illumination the assembled cells had the following performance values; power efficiency 4.45%, open circuit voltage V_{OC} 750 mV, short circuit current I_{SC} 8.31 mA, fill factor 71%. The absorption coefficient of the sensitized TiO_2 layers were estimated from IPCE values taking into consideration reflections due to the TiO_2 substrate.

Photocurrent transients were measured in a custom-built Faraday cage dark box. The measured photocurrents from the cells were cross referenced with a calibrated photodiode to thus ensure that the photon flux values were accurate. The cells were illuminated with a 532 nm laser diode and the light was switched on or off with a fast shutter. The photon flux was varied using neutral density filters, and defocused to illuminate the cell homogeneously. The currents were measured using a Femto DLPCA 200 current amplifier and recorded on a digital oscilloscope to give 0.2 μs time resolution. With an input impedance of 50 Ω and the blocking layer–electrolyte interface having a double layer capacitance of about 1 μFcm^{-2} the geometric RC time constant for the 0.196 cm^2 cells was 10 μs. For the light

on transients it was found that 60 s was sufficient time for the cells to re-equilibrate in the dark so that filled traps would not affect the rise time behaviour.

Theory

Electron transport to the collecting anode in these cells is driven by the concentration gradient of electrons in the conduction band of the oxide, since the electrical field in the bulk of the nanostructured electrode is negligible[9] as a consequence of screening by the high ionic strength electrolyte.

The ideas behind our two timescale Monte Carlo method are illustrated in Fig. 2. An electron diffusing through TiO_2 grains moves by a random walk in which it is scattered by interactions with phonons or other electrons. The time between scattering events can be obtained from the mobility of electrons in crystalline anatase TiO_2 and is 2 fs. The distance travelled in that time is ~0.1 nm so an electron will perform a random walk with many steps inside a grain before either encountering a grain neck where it could transfer to another grain, or a trap. In a fine scale simulation through a series of such random walks a list of possible electron behaviours (trap encounters and the grain in which the electron ends up) is generated over a time scale of 0.2 ns.

In the coarse scale simulation, if an electron is recorded as having encountered a trap in the fine scale simulation, then a trap energy E_T is selected randomly according to

$$E_T = k_B T_c \ln(R) \qquad (3)$$

where R is a random number chosen from a uniform distribution between 0 and 1.

Then, the trap occupancy at this energy is evaluated from

$$f = \left[1 + \exp\left(\frac{E_T - E_{F,redox}}{k_B T}\right)\right]^{-1} \qquad (4)$$

If f exceeds R_f where R_f is a random number chosen from a uniform distribution between 0 and 1, the trap is assumed to be full, otherwise the residence time for electrons falling into this trap is the inverse detrapping rate k_d^{-1} where

$$k_d = \frac{k_t N_c}{N_{t,0}} \exp\left[-\frac{E_C - E_T}{k_B T}\right] \qquad (5)$$

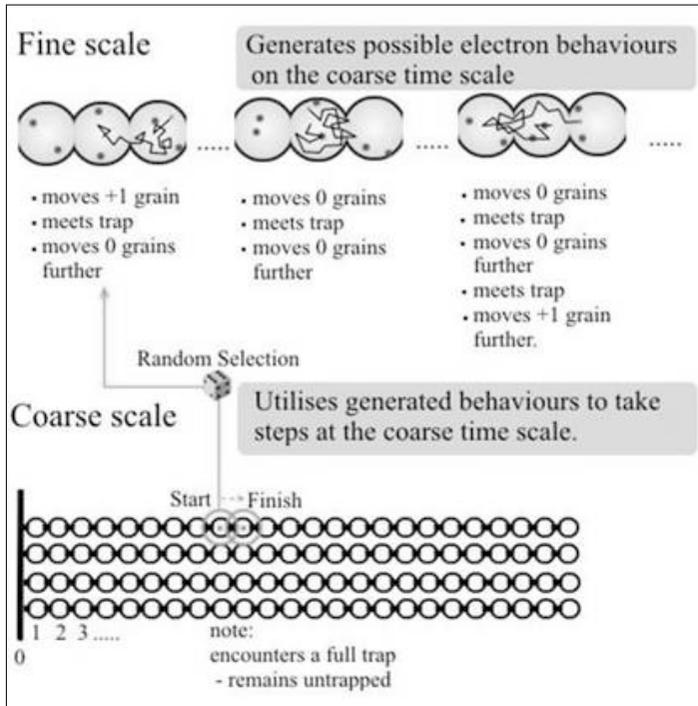and the trapping rate k_t is obtained from the trap radius R_{trap}, D_0 and $N_{t,0}$ from

Fig. 2. Schematic diagram demonstrating the two time-scale Monte Carlo method.

$$k_t = 4\pi R_{trap} D_0 N_{t,0} \qquad (6)$$

Then the coarse scale simulation randomly selects one of the possible behaviours from the list and moves the electron accordingly. A more complete description of the two-scale approach is provided elsewhere.[6]

For simplicity, back reactions have been neglected. Electron–electron interactions are largely screened out by the ions in the electrolyte and by the large static dielectric constant of TiO_2 and so are ignored here. They are unlikely in any case to be important at solar intensities which correspond to a few electrons being injected per grain.

As the Monte Carlo simulations take more than a day to run on a fast workstation, we have also developed a continuum model that explicitly includes traps. Here, the grains are considered as a homogeneous material and so a one-dimensional model can be used to find the conduction band electron density profile $n_c(x,t)$ where x is the distance from the electron extracting electrode and t is the time using the continuity equation

$$\frac{\partial n_c}{\partial t} = \frac{\partial^2 n}{\partial x^2} + \alpha I_0 \exp[-\alpha x]$$
$$- k_0(n_c - n_{eq}) - \frac{\partial n_t}{\partial t} \qquad (7)$$

Here, α is the absorption coefficient of the sensitized layer, $I_0(t)$ is the incident photon flux corrected for reflection losses, n_t the trapped electron density and k_0 the pseudo-first-order rate constant for the transfer of electrons from the conduction band to redox species (usually I_3^-), is the reciprocal of the conduction band electron lifetime, τ_0. Electron transfer *via* surface states has been neglected.[1] The continuity equation for the trap occupation probability f is

$$\frac{\partial n_t}{\partial t} = N_{t,0}\left\langle\frac{\partial f}{\partial t}\right\rangle = \left\langle k_t n_c (1-f) - k_d N_{t,0} f\right\rangle \qquad (8)$$

where the angular brackets denote an average over all trap energies weighted by $g(E_T)$. For illumination from the anode side $(x = 0)$, the boundary conditions are

$$k_{ext} n_c(0) = D_0 \left.\frac{dn_c}{dx}\right|_{x=0}, \quad \left.\frac{dn_c}{dx}\right|_{x=d} = 0 \qquad (9)$$

where k_{ext} is the first-order heterogeneous rate constant for electron extraction at the anode.

Results

We assumed that the intensity $I_0(t)$ increased sharply (*i.e.* was a step function) at the start (light on) to a steady state value I_{0ss} and decreased sharply at the end (light off) of the pulse. Measured transient currents $J_{photo}(t)$ for the light on and light off cases are compared with Monte Carlo and continuum model predictions in Fig. 3 for the parameter values in the Table. Fig. 3 shows that good agreement is obtained between the three sets of data except at short times for the transients where light is switched on. We had to use a smaller value of D_0 in the continuum model than in the Monte Carlo simulations to allow for the slowing down of electrons at the grain necks which is included explicitly in the Monte Carlo simulations. It is encouraging that a good fit was obtained for trap distribution parameters obtained from charge extraction measurements.[4] We find in both Monte Carlo and continuum models that as either T_c or $N_{t,0}$ is increased, it takes longer before a significant increase in J_{photo} is observed,[10] consistent with the idea that either more deep traps or a greater trap density will slow down the electrons.

Fig. 4 shows that the rise time t_{rise} is longer than the fall time t_{fall} at all intensities. This behaviour has a straightforward explanation within the MT model. When light is switched on, the traps are all empty initially since $_nE_F$ is equal to $E_{F,redox}$. Thus, the detrapping time is long and most of the photogenerated electrons fill the traps and do not come out so the response time of the cell to the changing illumination is slow. As time goes on, $_nE_F$ rises in the bulk of the cell towards a value determined by I_{0ss} (although the boundary condition in Eqn. (9) ensures that $_nE_F$ drops to a low value at the extracting electrode) and the electrons detrap more rapidly, thus the time taken for them to reach the extracting electrode decreases and J_{photo} increases. There is a discrepancy between

Table. Parameter values used in experimental measurements and the Monte Carlo (MC) and continuum model (cont) predictions shown in Fig. 3. The brackets show the model for which that parameter value was used where these differed.

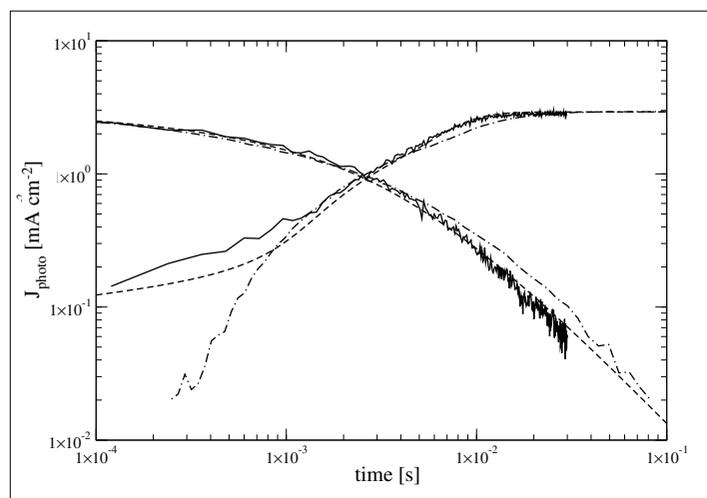|	
α	2.4×10^3 cm^{-1}
d	5 μm
T	298 K
D_0 (MC)	0.4 cm^{2}s^{-1}
D_0 (cont)	0.01 cm^{2}s^{-1}
N_C	1.0×10^{21} cm^{-3}
$E_{F,red}$	0.95 eV
$N_{t,0}$	2.28×10^{19} cm^{-3}
T_c	903 K
k_{trap} (MC)	1.5×10^{12} s^{-1}
k_{trap} (cont)	3.0×10^{10} s^{-1}
R_{trap}	0.1 nm
k_0	1.0×10^2 s^{-1}
k_{ext}	1.0×10^4 s^{-1}
I_{0ss}	2.61×10^{16} cm^{-2}s^{-1}

Fig. 3. Transient photocurrent density J_{photo} (mAcm^{-2}) *vs* time *t* (s). The lines with a large value on the left of the figure are for light off, *i.e.* at the end of the illumination pulse, and on the right of the figure are for light on, *i.e.* the start of the illumination pulse. In both cases, chained lines: experimental data, solid lines: Monte Carlo predictions, dashed lines: continuum model predictions.
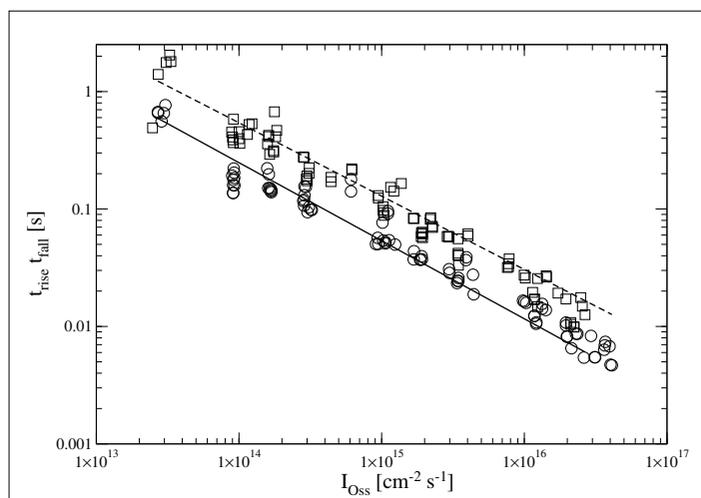
Fig. 4. Squares: measured rise time t_{rise}, *i.e.* the time taken for the current to go from 10% to 90% of its steady state value (light on) in s. These times are plotted as a function of the steady state intensity I_0 in cm^{-2}s^{-1}. The dashed line shows a fit by eye to t_{rise} that has the form $t_{rise} = 3.0 \times 10^8 I_0^{-0.6245}$. Circles: measured fall time t_{fall} *i.e.* the time taken for the current to go from 90% to 10% of its steady state value (light off) in s. The solid line shows a fit by eye to t_{rise} that has the form $t_{rise} = 5.0 \times 10^8 I_0^{-0.6646}$.

both models and experiment at times less than 1 ms when illumination is turned on, which may be due to extra charging effects or inhomogeneities not considered in the model such as a large concentration of traps near the extracting electrode or a barrier to extraction. By contrast, when the light is switched off, the traps are initially all full and there is a short time for them to detrap and so reach the extracting electrode, leading to a faster response time.

Summary

We have shown that the multiple trapping model can explain experimental data on transient photocurrents in response to large amplitude changes in illumination, but only if traps are explicitly considered.

Received: October 12, 2007

[1] M. Gratzel, *Phil. Tran. Royal. Soc. A* **2007**, *365*, 993.
[2] L. M. Peter, *J. Phys. Chem. C* **2007**, *111*, 6601.
[3] P. E. de Jongh, D. Vanmaekelbergh, *Phys. Rev. Lett.* **1996**, 3427.
[4] M. Bailes, P. J. Cameron, K. Lobato, L. M. Peter, *J. Phys. Chem. B* **2005**, *109*, 15429.
[5] N. Kopidakis, K. D. Benkstein, J. van de Lagemaat, A. J. Frank, Q. Yuan, E. A. Schiff, *Phys. Rev. B* **2006**, *73*, 045326.
[6] M. J. Cass, A. B. Walker, D. Martinez, L. M. Peter, *J. Phys. Chem. B* **2005**, *109*, 5100.
[7] A. B. Walker, L. M. Peter, M. J. Cass, P. J. Cameron, D. Martinez, *J. Mat. Chem.* **2005**, *15*, 2253.
[8] A. B. Walker, L. M. Peter, K. Lobato, P. J. Cameron, *J. Phys. Chem. B* **2006**, *110*, 25504.
[9] L. M. Peter, *Phys. Chem. Chem. Phys.* **2007**, *9*, 2630.
[10] A. B. Walker, D. Martinez, unpublished results **2006.**