

Electron and electrolyte transport in the dye sensitized nanocrystalline cell

F Qiu[†], A B Walker[†], A C Fisher^{*}, A D Savin^{*} and L M Peter^{*}

[†]Department of Physics, ^{*}Department of Chemistry
University of Bath, Bath BA2 7AY, UK

Introduction

One of the puzzling features of dye-sensitised nanocrystalline solar cells is the slow electron transport in the titanium dioxide phase. The available experimental evidence as well as theoretical considerations suggest that the driving force for electron collection at the substrate contact arises primarily from the concentration gradient, ie the contribution of drift is negligible. The transport of electrons has been characterised by small amplitude pulse or intensity modulated illumination [1]. Here, we show how the transport of electrons in the dye-sensitised cell can be described quantitatively using trap distributions obtained from a novel charge extraction method [2]. In addition we will present extensions to the model to establish the influence of electrolyte transport and reaction processes.

Theory

Electrons injected by the photoexcited dye may move by random walk to a vacant trap site, where they will be localised for a period of time that depends on the trap depth relative to the conduction band. Electrons may also be transferred to the oxidised dye D⁺, but this process is usually unimportant if dye regeneration from D⁺ by electron transfer from I⁻ is sufficiently fast. Electrons may also be transferred across the solid/electrolyte interface to I₃⁻ ions, resulting in formation of I⁻ ions. This process represents a loss of pathway that decreases the efficiency for photocurrent generation. Here it has been assumed that the reaction of electrons with I₃⁻ can take place either via the conduction band or via electron transfer from surface traps. In both cases, the reaction is taken to be either first or second order in electron density [1]. Electrons reaching the substrate can pass into the conduction band of the anode.

The continuity equation for the conduction band electron density n as a function of position x along the cell starting from the anode and time t is

$$\frac{\partial n}{\partial t} = D_{bare} \frac{\partial^2 n}{\partial x^2} - k_{cb}(n^\mu - n_{dark}^\mu) + \alpha I_0 e^{-\alpha x} - I_{trap}$$

Here the first term is the diffusion current [D_{bare} is the diffusion coefficient without traps], the second term the back reaction with I₃⁻ ions from the conduction band [k_{cb} is the reaction rate, n_{dark} is n if I_0 is zero where I_0 is the light intensity, and $\mu = 1$ for 1st order, $\mu = 2$ for 2nd order reactions], and the third term is the generation of conduction electrons through electron injection into the TiO₂ particles, [α is the absorption coefficient]. The fourth term

$$I_{trap} = \langle k_{trap} n(1-f) - k_{detrapp} N_{t0} f \rangle$$

is the net trapping rate for a trap density N_{t0} , trapping rate k_{trap} and detrapping rate $k_{detrapp}$. $\langle A \rangle$ represents an average over the trap distribution for any quantity A ;

$$\langle A \rangle = \int_{-E_g}^0 dE_T s(E_T) A(E_T) \quad ,$$

$$s(E_T) = \frac{\beta}{k_B T} \exp\left[\frac{\beta E_T}{k_B T}\right]$$

is the probability of finding a trap in the energy range $E_T \rightarrow E_T + dE_T$. The form chosen is consistent with the trap

distribution deduced in [2]. We obtain the probability of trap occupation f from solving

$$\left\langle \frac{\partial f}{\partial t} \right\rangle = \langle \frac{k_{trap} n}{N_{t0}} (1-f) - k_{detrapp} f \rangle - \frac{k_{tb}}{N_{t0}} (n_{trap}^\mu - n_{dark}^\mu)$$

where the average occupied trap density $n_{trap} = N_{t0} \langle f \rangle$, k_{tb} is the rate for the back reaction of the trapped electrons with the I₃⁻ ions and n_{dark} is n_{trap} if I_0 is zero. A similar model is used for electrolyte transport.

Results

The results for the IPCE and U_{photo} shown in figure 1 are encouragingly close to the experimental data reported in [1] – note that U_{photo} in [1] is in V not mV. The IPCE is sensitive to the value of β . With $\beta = 0.1$, corresponding to a much broader trap distribution than $\beta = 0.2$, the IPCE is much smaller. The results for n , f and the extracted charge, photovoltage and photocurrent from transient and modulated light intensities for various trap distributions will be presented and compared with experimental data. We will discuss if the back reaction is more likely to be 1st or 2nd order and present results for electrolyte transport.

Conclusions

We have predicted how the photocurrent and photovoltage vary with the trap distribution with a 2nd order reaction of electrons with I₃⁻ and the results for the IPCE and dc photovoltage show good agreement with experiment. Our model can be used to elucidate the kinetics of the back reaction with I₃⁻.

References

1. AC Fisher, LM Peter, EA Ponomarev, AB Walker, KGU Wijayantha *J Phys Chem B* **104** 949 (2000)
2. NW Duffy, LM Peter, RMG Rajapakse, KGU Wijayantha *Electrochem Comm* **2** 658 (2000)

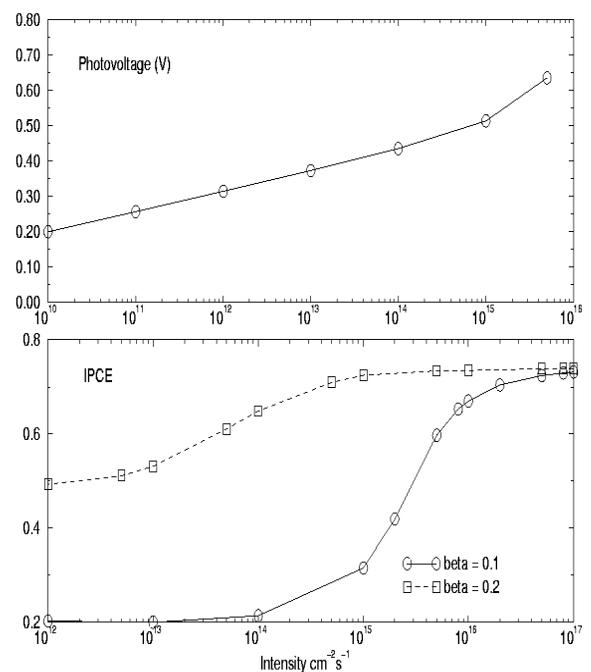


Fig 1. Predicted steady state photovoltage (V) (top panel) and IPCE (bottom panel) dependence on I_0 ($\text{cm}^{-2} \text{s}^{-1}$) for a 2nd order back reaction. Top panel $\beta = 0.2$ Bottom panel: $\beta = 0.1$ (solid line), $\beta = 0.2$ (dashed line).