Modelling of electron transport in the dye sensitized nanocrystalline cell

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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 the density of states function from traps obtained using a novel charge extraction method [2].

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 Γ^- is sufficiently fast. Electrons may also be transferred across the solid/electrolyte interface to I_3^- ions, resulting in formation of Γ^- 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 I_3^- can take place either via the conduction band or via electron transfer from surface traps. In both cases, the reaction is taken to be 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 hence

$$\frac{\partial n}{\partial t} = D_{bare} \frac{\mathrm{d}^2 n}{\mathrm{d}x^2} - k_{c\delta 2} (n^2 - n_{dark}^2) + \alpha I_0 e^{-\alpha t} - k_{tc\delta 2} (n^2 - n_{trap}^2) \tag{1}$$

Here the first term is the diffusion current $[D_{bare}$ is the diffusion coefficient without traps], the second term the back reaction with I_3^- ions from the conduction band $[k_{cb2}$ is the rate for this reaction, n_{dark} is n if I_0 is zero where I_0 is the light intensity], the third term is the generation of conduction electrons through electron injection into the TiO₂ particles, [α is the absorption coefficient] and the fourth term is the same as the second term but from traps $[k_{tb2}$ is the rate for this reaction] and n_{trap} the density of trapped electrons] and n_{trap} is obtained from the trap occupation probability f using

$$n_{trap} = N_{t0} < f >= N_{t0} \int_{-E_g}^{0} dE_T s(E_T) f(E_T); \qquad s(E_T) = \frac{\beta}{k_B T} \exp\left[\frac{\beta E_T}{k_B T}\right]$$
(2)

where $s(E_T)dE_T$ 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 *f* from

$$\frac{\partial n_{trap}}{\partial t} = N_{t0} \left\langle \frac{\partial f}{\partial t} \right\rangle = \langle k_{trap} n(1-f) - k_{detrap} N_{t0} f \rangle - k_{t02} \left(n_{trap}^2 - n_{dark}^2 \right)$$
(4)

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 and U_{photo} are sensitive to the value of β ; with $\beta = 0.1$ corresponding to a much broader trap distribution, both quantities are much smaller. The results for f and for the response to the modulated intensity will be presented in my talk.

Conclusions

We have predicted how the photocurrent and photovoltage vary with the trap distribution assuming a second order reaction of electrons with I_3^- and the results at least for the IPCE and dc photovoltage show good agreement with experiment.



Fig 1: Variation with I_0 [in units of m⁻²s⁻¹] of the incident photon-to-current conversion efficiency (IPCE) (top panel), dc photovoltage U_{photo} [in units of V] (bottom panel).

References

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