Modelling Electrons in the Dye-Sensitized Nanocrystalline Solar Cell (DSC)

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This paper reviews current understanding of the roles of interfacial electron transfer, electron transport and trapping in determining voltage and current in DSCs and highlights areas where further work is needed.

The basic principles of the DSC are well known. A light-harvesting dye is adsorbed on a porous nanocrystalline TiO_2 film permeated by the iodide/tri-iodide redox electrolyte that regenerates the dye following electron injection from the excited state into the TiO_2 conduction band. Injected electrons reach the contact by a random walk process involving multiple trapping at states in the bandgap of the oxide. The DSC relies on establishing a photostationary condition in which the transfer of electrons in the TiO_2 to I_3^- is slow, so that a high concentration of conduction band electrons can generate a photovoltage, whereas electron transfer to I_3^- must be fast at the regenerating electrode to avoid voltage losses on load. The I_3^-/I^- couple is unusual in providing this strong kinetic asymmetry. Reduction of I_3^- at platinum is fast, since it proceeds via dissociative chemisorption of I_2. By contrast, the reduction of I_3^- at wide bandgap metal oxides is slow, involving initial reduction of I_3^- to $I_2^{-\cdot}$, which can then undergo a second electron transfer to form I^- or disproportionate into I_3^- and I^-.

Electron transport in DSCs involves a trap-limited random walk process in which photoinjected electrons are shielded by the high ionic strength electrolyte. The generation-collection problem is formulated using the 1-D continuity equation

$$\frac{\partial n(x,t)}{\partial t} = \alpha I_0 e^{-\alpha x} + D_n \frac{\partial^2 n(x,t)}{\partial x^2} - k_n\left[n(x,t) - n_0\right] \qquad 1)$$

$n(x,t)$ is the density of electrons *in the conduction band* of the oxide, n_0 is the equilibrium (dark) electron concentration, α is the absorption coefficient of the dye-sensitized medium, I_0 is the incident photon flux corrected for reflection losses, D_n is the diffusion coefficient of free electrons and k_n is the first order rate constant for their back reaction of electrons with I_3^-. The lifetime of electrons, τ_n, is given by the reciprocal of k_n. Competition between collection and back reaction of electrons can be expressed in terms of the electron diffusion length L_n:

$$L_n = \sqrt{D_n \tau_n} \qquad 2)$$

Efficient electron collection is obtained only if the electron diffusion length exceeds the film thickness, which is typically of the order of 10 μm.

Small amplitude methods such as intensity modulated illumination have been used to determine 'apparent' values of D_n and τ_n. However, these are not the true values characteristic of conduction band electrons because the relaxation time constants for the photocurrent and photovoltage are affected by the trapping/detrapping of electrons. D_n (apparent) increases with light intensity whereas τ_n (apparent) decreases. The apparent electron diffusion length, on the other hand, is almost independent of intensity over a wide range of intensity. This has been observed both for electrolyte cells and cells using an organic hole conductor. An explanation of these experimental observations has been provided by Bisquert and Vikhrenko[1], who introduced the *quasi-static assumption* that the free and trapped electrons remain in a common equilibrium when the system is displaced away from equilibrium by some perturbation. The quasi-static condition relates the time dependence of the conduction band electron density $\partial n_c/\partial t$ to the corresponding rate of change of the density of trapped electrons $\partial n_t/\partial t$:

$$\frac{\partial n_t}{\partial t} = \frac{\partial n_t}{\partial n_c}\frac{\partial n_c}{\partial t} \qquad 3)$$

The 'apparent' values of the electron diffusion coefficient and electron lifetime are given respectively by

$$4) \qquad \tau_n = \left(\frac{\partial n_t}{\partial n_c}\right)\tau_0 \quad \text{and} \quad D_n = \left(\frac{\partial n_c}{\partial n_t}\right)D_0$$

Here D_0 is the diffusion coefficient of electrons in the conduction band of the TiO_2, which has been estimated from time-resolved microwave conductivity measurements to be 0.05 $cm^2\ s^{-1}$ for compact anatase films. τ_0 is the reciprocal of the first order rate constant for reaction of conduction band electrons with tri-iodide ions. It follows from these expressions that the electron diffusion length is expected to be *independent of intensity*:

$$L_n = \sqrt{D_n \tau_n} = \sqrt{D_0 \tau_0} \qquad 5)$$

The electron trapping states in nanocrystalline TiO_2 appear to be distributed exponentially in energy, with a higher density of shallow traps near the conduction band and a lower density of deeper traps.

The distribution can be written in the form 6)

$$s_t\left({}_nE_F - E_{F,redox}\right) = s_t\left(0\right)e^{\left[\frac{\beta\left({}_nE_F - E_{F,redox}\right)}{k_BT}\right]} = s_t\left(0\right)e^{\left[\frac{\beta qU_{photo}}{k_BT}\right]}$$

Here $s_t(E)$ is the density of states function for the electron traps, $s_t(0)$ is the value of the density of states function at an energy corresponding to the redox Fermi level of the iodide/tri-iodide redox couple ($E_{F,redox}$) and ${}_nE_F$ is the quasi Fermi level of electrons which describes the occupancy of trap and conduction band states under illumination. ${}_nE_F$ is related to the photovoltage U_{photo} by

$${}_nE_F - E_{F,redox} = qU_{photo} \tag{7}$$

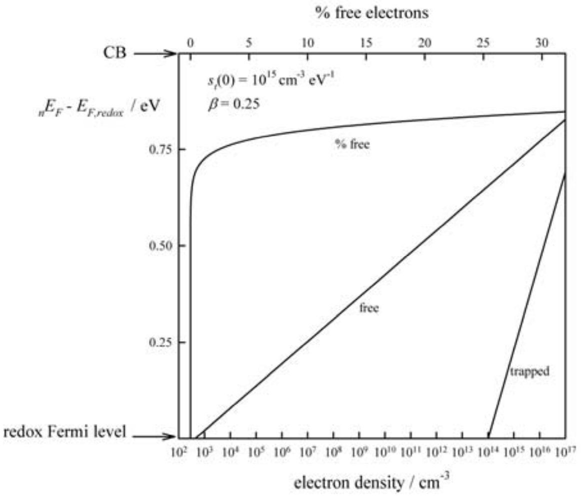
In general, the derivative $\partial n_t/\partial n_c$ is related to any density of states function for electron traps $s_t(E)$ by

$$\frac{\partial n_t}{\partial n_c} = \frac{k_BT}{n_c}s_t(E) \tag{8}$$

where n_c, the conduction band electron density, is determined by the illumination intensity, since

$$\frac{n_c}{n_{c,dark}} = \mathrm{e}^{\frac{qU_{photo}}{k_BT}} \quad \text{and} \quad n_{c,dark} = N_c\,\mathrm{e}^{-\frac{E_c - E_{F,redox}}{k_BT}} \tag{9}$$

Figure 1 shows how raising the quasi Fermi level affects the free and trapped electron densities, and Figure 2 shows how the quasistatic electron distribution affects the values of D_n and τ_n.



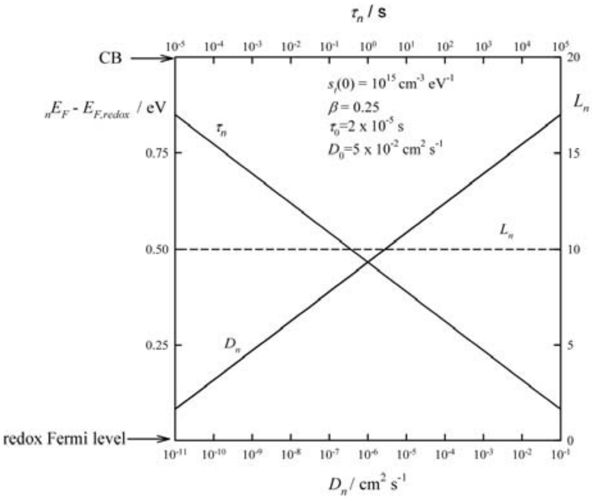


Figure 1 Figure 2

The concentration profile for conduction band electrons must be derived from the solution of the continuity equation by using D_0 and τ_0 rather than the 'effective' values. If we use a value of D_0 = 0.05 cm^2 s^{-1} [36], the conduction band lifetime τ_0 must exceed 2 × 10^{-5} s in order to give an electron diffusion length greater than 10 µm, as required for an efficient cell. Using these values, the profile of free electron density can be calculated for short circuit conditions if α, I_0 and k_{ext} is known. A value of $k_{ext} = 10^5$ cm s^{-1} has been used here to correspond to diffusion controlled extraction of electrons at the contact. In the absence of back reaction via the conducting glass substrate, open circuit conditions are defined by setting $k_{ext} = 0$.

The local electron density in the conduction band defines the electron quasi Fermi level since

$$n_c = N_c \exp\left[\frac{{}_nE_F - E_c}{k_BT}\right] \tag{10}$$

In the dark, the conduction band electron density is determined by the redox Fermi level $E_{F,redox}$.

$$n_{c,dark} = N_c \exp\left[\frac{E_{F,redox} - E_c}{k_bT}\right] \tag{11}$$

so that

$$n_c = n_{c,dark}e^{\frac{qU_{photo}}{k_Bt}} \tag{12}$$

since the upward displacement of the electron Fermi level under illumination defines the photovoltage, U_{photo}, of the cell: $qU_{photo} = {}_nE_F - E_{F,redox}$ 13)

Since the occupation of electron traps is also defined to the quasi Fermi level, the profile o trapped electrons can be calculated by integrating the DOS function (eq. 6) up to the quasi Fermi level.

Figure 3 illustrates the profiles of free and trapped electrons across a ten micron thick sensitized TiO_2 layer under short circuit conditions. In this calculation, the incident photon flux (10^{17} cm^{-2} s^{-1}) corresponds approximately to 1 sun, and the absorption coefficient (2500 cm^{-1}) is typical for an optimized cell in the green part of the spectrum. The figure also shows how the quasi Fermi level varies across the film. Figure 4 shows the corresponding profiles for the open circuit case. It can be seen that the displacement of the quasi Fermi level at the contact corresponds to a photovoltage of just over 0.7 V, which is a typical value for an efficient cell. Interestingly, the calculated density of trapped electrons in the bulk of the film is rather similar under short circuit and open circuit conditions. Base on a mean particle size of 30 nm and a porosity of 50%, one can estimate the number of electrons per particle in the bulk region under 1 sun illumination as 2-3 per particle at short circuit and 3-5 per particle at open circuit.

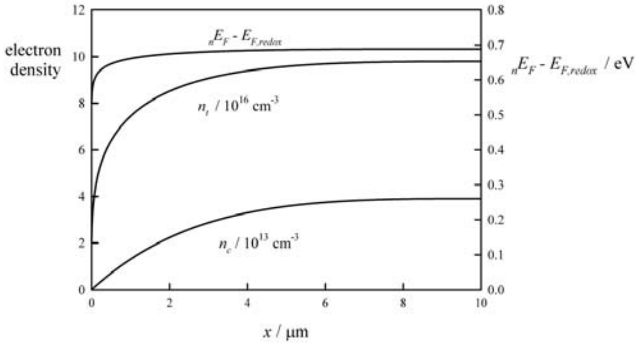


Figure 3. Profiles of free and trapped electrons (short circuit)

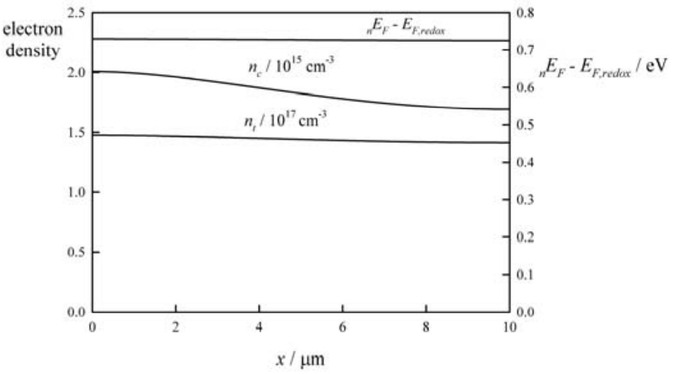


Figure 4. Profiles of free and trapped electrons (open circuit)

The preceding discussion shows that trapping influences electron transport and back reaction in such a way that the electron diffusion length remains constant. In practice, it is possible to fabricate cells that fulfil the condition $L_n > d$, so that the IPCE is determined primarily by the efficiencies of light harvesting and charge injection. The short circuit current can be improved by utilizing scattering particle to enhance the red response of the dye. In addition, dyes with better near IR absorbance promise to harvest a larger fraction of the solar spectrum. The objective of research in this area is to obtain short circuit current densities of around 30 mA cm^{-2} to compete with thin film photovoltaic devices like copper(gallium) indium diselenide (CIGS) solar cells, which have band gaps matched almost perfectly to the AM 1.5 solar spectrum.

Conclusions

Dye-sensitized nanocrystalline cells demonstrate that efficient solar cells can be fabricated from low cost materials by using a novel approach to the problems of light harvesting and current collection. The physics and chemistry of the DSC offer a challenging area where much remains to be done before stable, cheap solar cells can be ready for the market. Before the technological development of DSCs can move forwards, progress towards better understanding will need to be made by focussing on key fundamental questions, some of which have been raised in the present paper.

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Appendix

The following values were used in the calculations except where noted otherwise.
$T = 298K$. $N_c = 1 \times 10^{20}$ cm^{-3}. $E_c - E_{F,dark} = 1.0$ eV. $s_t(0) = 10^{15}$ cm^{-3} eV^{-1}. $\beta = 0.25$. $D_0 = 0.05$ cm^2 s^{-1}.
$\tau_0 = 2 \times 10^{-5}$ s. $k_{ext} = 1 \times 10^5$ cm s^{-1} (short circuit). $k_{ext} = 0$ (open circuit).

References

1. Bisquert, J. Vikhrenko, V. S . *Journal of Physical Chemistry B* **2004**, *108*, 2313.