Monte Carlo simulation of electron transport through nanocrystalline TiO_2 in dye sensitized solar cells (Grätzel cells)

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Abstract

Grätzel cells are based on a thin film of dye sensitized nanocrystalline TiO_2 interpenetrated by a redox electrolyte. Photoexcitation of the dye is followed by fast (less than 100fs) electron injection into the conduction band of the TiO_2 nanoparticles. The injected electrons travel through the nanocrystalline TiO_2 to the anode. Electron transport is slowed by trapping in surface and/or bulk states. Detrapping from these states competes with the back reaction of electrons with triiodide ions in the electrolyte. The back reaction causes electrons to be removed from the circuit and so reduces efficiency. The requirement to pass through grain necks also slows the electron transport, increasing the likelihood of back reactions occurring. We employ a Monte Carlo simulation to investigate the effects on electron transport of the connectivity. We use a multi-scale simulation method to model the response to a pulse of optical illumination; here the transient current and charge exiting the cell. Our main result is that for small inter-grain necks, transport through the film is slowed considerably. This effect is more pronounced when traps are present, as trapping competes with transfer between grains.

Dye sensitized nanocrystalline solar cells (Grätzel cells) have shown great promise because they are comprised of low cost materials and perform well under indirect radiation [1]. They are based on a thin film of porous nanocrystalline TiO_2 coated with a dye using a ruthenium complex that harvests the solar energy flux. Photoexcitation of the dye is followed by fast electron injection into the conduction band of the TiO_2 nanoparticle electrode. The electrons then travel through the TiO_2 to the collecting contact. The oxidized dye reacts with I^- ions in the electrolyte, producing I_3^- which diffuses to the Pt coated cathode where it is reduced to complete the cycle. The efficiency with which the incident photon flux is converted into current is determined in part by the competition between electron transport and back reaction. Optimization of electron collection is therefore clearly important for any practical cell, regardless of whether it employs an electrolyte or another contacting phase such as a polymeric hole conductor.

Electron transport in the TiO_2 grains occurs by diffusion since the fields across the film are screened by the electrolyte and the small size of the particles does not support a built in field [2]. An electron diffusion coefficient D_{bare} of $1\times10^{-2}\mathrm{cm}^2\mathrm{s}^{-1}$ has been deduced from mobility data for single crystalline TiO_2 [3]. The effective diffusion coefficient for electrons D_{eff} has been shown to vary with grain morphology from measurements of intensity modulated photocurrent spectra for anatase and rutile TiO_2 grains [4]. In addition, D_{eff} has been shown to vary with the background illumination intensity I_0 as $I_0^{0.68}$ [5]. Hence, the transit time for electrons across the films is also sensitive to I_0, being several minutes at low light levels and ms at solar illumination intensities [6]. The major reason for such behavior is trapping and detrapping of the electrons. The detrapping time increases exponentially with the trap depth. As I_0 increases, so does the generated electron density, thus the traps fill up, so the electrons are only trapped in the shallower traps and they detrap much faster.

The results presented here assume transport occurs in the conduction band, punctuated by a series of trapping and detrapping events. It is assumed that traps are located on the surface of the particles and have energies following an exponential distribution. To understand the influence of the morphology on electron transport, we have made predictions of the transient current using a Monte Carlo simulation, in which the electrons execute a random walk through a chain of spherical grains with traps at the surface of the grains. To cope with time scales varying from fs (the time between scattering events in each grain) to ms (the time scale for the transient current), we have adopted a novel approach using a combination of short time-scale and long scale simulations described in detail in [7]. Here, unlike [7], we also look at grains which are connected with 4-fold coordination in 3-dimensions (3D).

Fig 1 shows that even without traps, the morphology can significantly affect the transport properties of the film. As the necks get wider their effect on the transport is reduced. Transport is faster for chains than with 3D

connectivity due to the reduced dimensionality in the chain system. Fig 2 shows that the shape of the transient current curve is altered by by comparing the transient current with and without traps. Trapping which reduces the change in gradient with time. Without traps, it is possible to fit the Monte Carlo predictions for $J(t)$ to a curve deduced from an analytical expression with a single D_{eff}, but when traps are introduced, the change in the shape of the curves makes this impossible.

References

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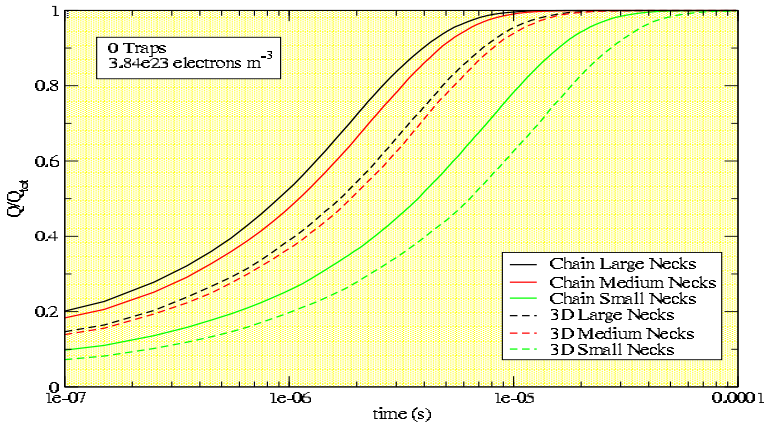

Figure 1: Total charge that has left the film as a function of time normalized to the total charge created through illumination. Solid curves are for particles in chains and dashed curves for 3D: black (large), red (medium), green (small) necks subtending 1.34,0.62,0.05 rad respectively.

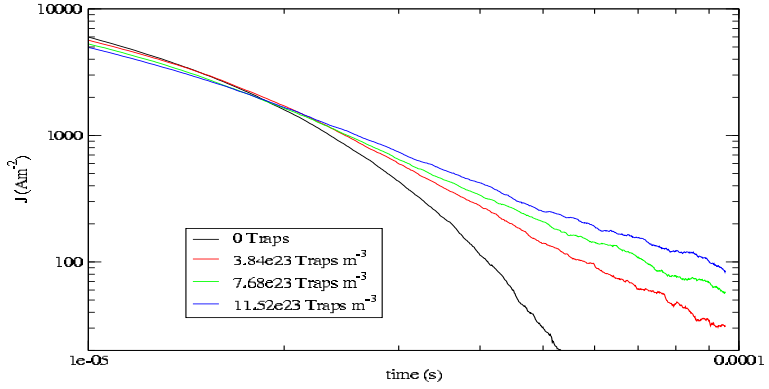

Figure 2: Transient currents for grains arranged in chains. The grains have small necks, subtending 0.05 rad. An initial electron concentration of $7.68\times10^{23}\mathrm{m}^{-3}$ in the chain system is assumed and the trap concentration takes the values 3.84,7.68 and 11.52 $\times10^{23}\mathrm{m}^{-3}$.