Barrier model for nanostructured dye-sensitized solar cells

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The charge transport properties, potential – charge dependence, and recombination processes in nanostructured dye-sensitized solar cells are most frequently described using trapping – detrapping models. These models usually assume an exponential distribution of localized electronic states below the conduction band edge. Conduction band electrons can trap in these states and trapped electrons can detrap through thermal activation. The result is that the concentration of conduction band electrons is only a small fraction of the total electron concentration in the solar cell. This can explain the small and light–dependent values observed for the diffusion coefficient of electrons in the nanostructured TiO_2 film and the observed relation between potential and charge.

Electron transport is well fitted using an exponential trap distribution with a distribution factor (β) of about 0.6 [1,2]. Voltage – charge measurements, however, yield β-values in the order of 0.2 [3]. This observation may invalidate the exponential trap model. Theoretical considerations of the trapping – detrapping model suggest that recombination should occur via the conduction band and not via the traps, which can only be true for traps located in the bulk of the nanoparticle. This seems to contradict the fact that nanocrystals in nanostructured film appear to be well-crystallized single crystals. A spectroelectrochemical investigation on nanostructured TiO_2 showed the presence of surface states located about 0.5 eV below the conduction band [4], which is too deep for them to be involved in a trapping / detrapping process. Finally, the spectrum of electrons in dye-sensitized nanostructured TiO_2 corresponds to conduction band elelctrons rather than trapped electrons [5].

We would like to propose a new model that *excludes* any traps, but still describes the properties of nanostructured dye-sensitized solar cells accurately: *the barrier model*. We assume that there are energy barriers associated with the grain boundaries between neighboring nanocrystals, see Figure 1. The contact area between crystals that is not perfectly (epitaxially) aligned may have charged defects, or may be amorphous in nature. Both possibilities will result in an energy barrier between the two crystals. Such barriers will significantly reduce the observed diffusion coefficient of conduction band electrons. Furthermore, it can be shown that accumulation of electrons in the nanostructured semiconductor film will reduce the activation energy for crossing the barrier. This can explain the observed light-intensity dependence of the electron transport.

An important consequence of the energy barriers is that they localize an electron in a single nanocrystal. The result is a discrete distribution of the electrons over the nanocrystals. In each nanocrystal the Fermi energy can be calculated from the electron occupancy. Under open-circuit conditions, the average energy of all nanocrystals corresponds approximately to the measured energy, i.e. the open-circuit potential of the solar cell. A simulation and experimental verification will be shown.
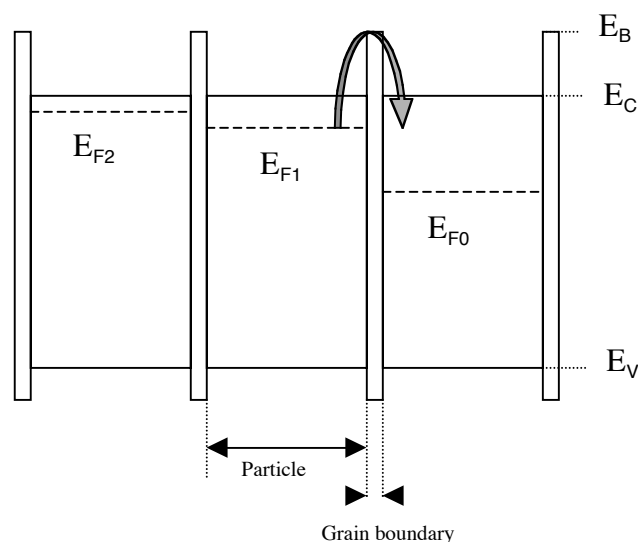

Figure 1: Schematic representation of the barrier model in a nanostructured semiconductor electrode. The grain boundaries are associated with energy barriers that localize an electron in a single nanocrystal. The Fermi level in a nanocrystal ($E_{F\,j}$) is determined its electron occupancy (j). $E_{F\,0}$ is equal to the redox level in the surrounding electrolyte. The arrow shows the thermally activated jump of an electron to a neighboring particle.

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