

The spatial electron distribution and its dynamics in the nanoporous TiO₂ network of a Dye Solar Cell

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Typical Dye Solar Cells (DSC) make use of nanoporous TiO₂ on one side as a host for the light absorbing dye molecules attached to its large surface. On the other side this material serves as the electron conductor. A key characteristic of the nanocrystalline TiO₂ is the abundance of traps for electrons. Traps are states for electrons in the forbidden zone in between the valence and the conduction band of a semiconductor. The existence of these traps is a consequence of irregularities in the bulk of the nano-crystals and the simple fact that they have a surface, i.e. in this case a lack of neighbour atoms. These traps have a great influence on the behaviour of the DSC with respect to the electron transport in the TiO₂ as well as the recombination between electrons in the semiconductor and ions in the electrolyte. The TiO₂ in a DSC is an insulator and becomes conductant only under illumination and the injection of electrons from the dye or by applying a bias voltage. That has several consequences for the functioning of the cell. Here, we want to show that it leads to an accumulation of charge carriers in the cell under short circuit conditions and thus to the built-up of an inner voltage across the TiO₂-network.

Two approaches were carried out to learn more about the influence of traps in the TiO₂ on the key characteristics of a DSC. The theoretical approach was to solve the differential equations describing the electron transport in a DSC under a certain generation regime. This was done both for short circuit and open circuit, respectively. A Shockley-Read-Hall formalism was applied to describe the processes of trapping and detrapping, i.e the capture of conduction band electrons into trap states and their release. The spatial distribution of the electron concentration in the conduction band of the TiO₂ in the steady-state can be obtained solving the following differential equation:

$$0 = \frac{\partial n_{\text{CB}}(x, t)}{\partial t} = -D \frac{\partial^2 n_{\text{CB}}(x, t)}{\partial x^2} + \text{gen}(x, t) - \text{rec}(x, t) - \text{trap}(x, t) - \text{detrap}(x, t), \quad (1)$$

where $\text{gen}(x, t)$ and $\text{rec}(x, t)$ stand for the generation and the recombination rates of the electrons, respectively and $\text{trap}(x, t)$ and $\text{detrap}(x, t)$ are the rates of capture of electrons by traps and their release back to the conduction band, respectively. All rates are in ($\text{cm}^{-3} \text{s}^{-1}$). The results are shown in Fig. 1, wherein x is the position in the TiO₂ having a total thickness of $d = 10 \mu\text{m}$. The TCO front electrode is located at $x = 0$.

The experimental approach included the method of charge carrier extraction as introduced by L. Peter and co-workers. The principle is to hold the illuminated cell under open circuit

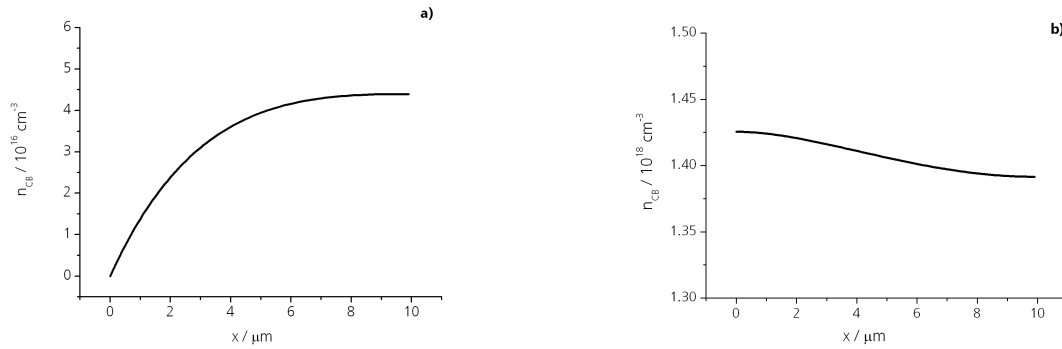


Figure 1: Spatial distribution of the conduction band electron concentration in the TiO_2 network under a) short circuit and b) open circuit conditions. The diffusion coefficient D was $5 \times 10^{-4} \text{ cm}^2\text{s}^{-1}$.

conditions. Then, first the illumination is quickly turned off. Hence, the open circuit voltage begins to decrease. After a variable delay time the cell is switched to short circuit. By means of integration of the transient current the total number of charge carriers that corresponds to a certain voltage of the cell in the moment of switching can be determined. Dividing this by the volume of the TiO_2 the charge carrier density in the semiconductor can be calculated. We found a surprisingly high charge carrier density stored in the nanoporous TiO_2 -network already under short circuit conditions. By comparison with measurements under open circuit conditions described above we could show that this charge carrier density corresponds to an average voltage of 550-600 mV . In other words, the high density of charge carriers under short circuit conditions is not just a consequence of a large number of occupied traps but also an effect of a poor conductivity in the TiO_2 . Together with the result from the theoretical description (Fig. 1a) we could therefore conclude that the voltage at the region far from the TCO front-electrode should be even higher.

Employing a third electrode being located at the end of the TiO_2 -layer we could achieve a direct proof for this observation and confirm our theoretical results. With this electrode, consisting of a thin, porous layer of titanium we could measure directly the voltage and so the electrochemical potential of the electrons at the far end of the TiO_2 -layer. The measurements confirmed fully our above deduced conclusions.