

## Direct Measurement of the Internal Electron Quasi-Fermi Level in Dye Sensitized Solar Cells Using a Titanium Secondary Electrode

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The spatial dependence of the electron quasi-Fermi level (QFL) in the interior of dye sensitized nanocrystalline solar cells (DSC) under short circuit conditions can be inferred from calculations based on a diffusive electron transport model. The calculations predict that the difference in the QFL between the electrolyte and contact sides of the TiO<sub>2</sub> layer under short circuit conditions at 1 sun could be as much as 0.5–0.7 eV. The predicted QFL profiles depend on assumptions made about energy positions, electron mobility, and the conduction band density of states. In this work, the position of the QFL at the electrolyte side of the dye sensitized TiO<sub>2</sub> film in a DSC has been measured using a thin passivated titanium contact deposited on top of the nanocrystalline TiO<sub>2</sub> by evaporation. The method allows changes in the electron QFL at all points on the *IV* characteristic of the cell to be monitored under dark and photostationary conditions. In addition, cells incorporating the titanium electrode can give information about the behavior of the QFL under dynamic conditions.

The available experimental evidence suggests that electron transport in dye sensitized nanocrystalline solar cells (DSC) occurs by diffusion of electrons in the conduction band in the nanocrystalline TiO<sub>2</sub> to the underlying fluorine doped tin oxide anode. For illumination through the substrate, the steady state profiles,  $n_c(x)$ , of free electrons across the nanocrystalline oxide film can be calculated by solving the continuity equation for different boundary conditions<sup>1–5</sup>

$$\frac{\partial n_c(x)}{\partial t} = \eta \alpha I_0 e^{-\alpha x} + D_0 \frac{\partial^2 n_c}{\partial x^2} - k_0(n_c - n_{eq}) = 0 \quad (1)$$

Here,  $\alpha$  is the absorption coefficient of the sensitized absorber layer,  $\eta$  is the quantum efficiency for electron injection,  $I_0$  is the incident photon flux corrected for reflection losses,  $D_0$  is the diffusion coefficient of electrons in the conduction band,  $k_0$  is the pseudo-first-order rate constant for the reaction of conduction band electrons with I<sub>3</sub><sup>−</sup>, and  $n_{eq}$  is the equilibrium density of electrons present in the dark.  $\tau_0 = k_0^{-1}$  corresponds to the lifetime of electrons in the conduction band in the absence of trapping/detrapping effects. It is known that the nanocrystalline TiO<sub>2</sub> in DSCs has a high density of electron traps that are distributed exponentially in the energy gap.<sup>6–9</sup> However, for stationary conditions, the local trap occupancy is constant, so that eq 1 does not contain terms to describe trapping and detrapping of electrons.

Values of  $\alpha$  and  $I_0$  are experimentally accessible, but quantitative solutions of eq 1 to obtain  $n_c(x)$  also require values for  $D_0$ ,  $k_0$ , and  $n_{eq}$ . Considerable uncertainty exists about the magnitudes of the first two quantities,<sup>10</sup> and  $n_{eq}$  depends on assumptions made about the density of states in the conduction

band and the difference between the conduction band and the redox Fermi level. Nevertheless, the electron density profiles predicted by eq 1 for short circuit conditions at 1 sun typically predict a large difference of the order of 0.5–0.7 eV in quasi-Fermi level between the anode contact, where the short circuit to the cathode pins it close the redox Fermi level, and the other side of the TiO<sub>2</sub> film, which is typically 5–10  $\mu\text{m}$  thick. Similar conclusions were reached by Würfel et al.<sup>11</sup> based on comparison of the trapped electron densities under open circuit and short circuit conditions. To test the validity of the diffusion model experimentally, it is necessary to devise methods that can give independent information about the free electron density profiles across the TiO<sub>2</sub> layers. Here, we show that the electron quasi-Fermi level can be probed on the side furthest from the anode by using a thin film of passivated titanium as a secondary electrode. This method, which was first reported by Würfel et al.,<sup>12</sup> allows direct comparison between theory and experiment for conditions ranging between short circuit and open circuit. The measurements have demonstrated that the electron quasi-Fermi level at this position is indeed over 0.5 eV under short circuit conditions at 1 sun. This narrows substantially the range of possible parameter values in eq 1.

### Theory

Taking the fluorine doped tin oxide (FTO) substrate contact as the origin ( $x = 0$ ) and assuming diffusion controlled electron exchange at the FTO|TiO<sub>2</sub> interface (the more general case of kinetically controlled electron exchange has been considered elsewhere<sup>3</sup>), eq 1 can be solved to give  $n_c(x)$  and the *IV* characteristic by using the boundary conditions

$$\left. \frac{dn_c}{dx} \right|_{x=d} = 0 \quad (2a)$$

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$$n_c(0+) \rightarrow n_{eq} e^{qU/k_B T} \quad (2b)$$

Here,  $x = 0+$  refers to the point close to the anode but outside any double layer region at the contact,  $d$  is the thickness of the nanocrystalline  $\text{TiO}_2$  film,  $n_0$  is the density of electrons at  $x = 0$ , and  $n_{eq}$ , the equilibrium density of electrons in the  $\text{TiO}_2$  in the dark, is given by

$$n_{eq} = N_C e^{-(E_C - E_{F,redox})/k_B T} \quad (3)$$

where  $N_C$  is the density of states in the conduction band.

The electron quasi-Fermi level,  $nE_F(x)$  is related to the local density of conduction band electrons,  $n_c(x)$ , by

$$n_c(x) = N_C e^{-(E_C - nE_F(x))/k_B T} \quad (4)$$

The flux of electrons at the contact,  $j(0)$ , can also be obtained as a function of voltage,  $U$ . It can be shown that the general expression for the  $IV$  characteristic takes a form analogous to the diode equation:<sup>2</sup>

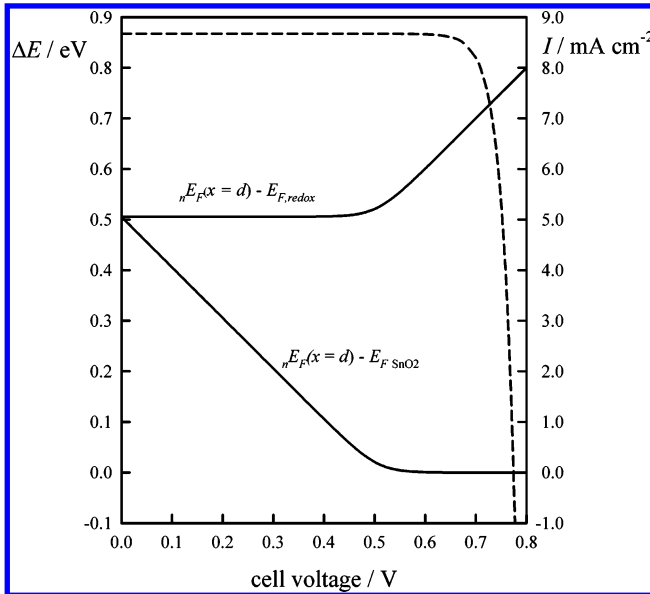
$$j(0) = qI(1 - e^{-\alpha d}) - q \frac{D_0 n_{eq} d}{L_n^2} (e^{qU/k_B T} - 1) \quad (5a)$$

where

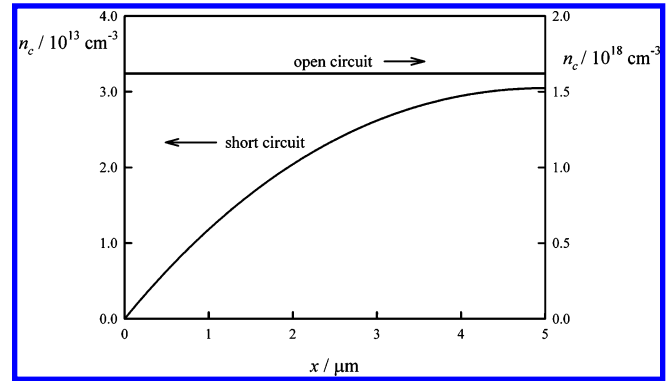
$$L_n = \sqrt{\frac{D_0}{k_0}} = \sqrt{D_0 \tau_0} \quad (5b)$$

is the electron diffusion length.

Figure 1 illustrates a typical  $IV$  characteristic calculated for illumination at 1 sun together with the corresponding variation of the quasi-Fermi level (QFL) at  $x = d$  relative to the redox Fermi level and the difference in QFL between  $x = d$  and  $x =$



**Figure 1.** Calculated  $IV$  characteristic and corresponding variation of the quasi-Fermi level at  $x = d$  relative to the redox Fermi level,  $E_{F,redox}$ , and relative to the Fermi level in the tin oxide substrate,  $E_{F,SnO_2}$ . Values used in the calculation: thickness of nanocrystalline  $\text{TiO}_2$  film,  $d = 5 \mu\text{m}$ ; diffusion coefficient of conduction band electrons,  $D_0 = 0.4 \text{ cm}^2 \text{ s}^{-1}$ ; conduction band density of states,  $N_C = 10^{21} \text{ cm}^{-3}$ ; rate constant for back electron transfer to oxidized species,  $k_0 = 10^2 \text{ s}^{-1}$ ; energy of the conduction band relative to the redox Fermi level,  $E_C - E_{F,redox} = 0.95 \text{ eV}$ ; incident photon flux,  $I_0 = 1.2 \times 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$ ; absorption coefficient,  $\alpha = 1200 \text{ cm}^{-1}$ ; temperature,  $T = 298 \text{ K}$ .



**Figure 2.** Profiles of conduction band electron density calculated for short circuit and open circuit conditions (note the different y scales for the two plots). The same values of the variables as those used for Figure 1 were used in the calculation.

0. Figure 2 shows the free electron density profiles across the  $\text{TiO}_2$  film calculated for short circuit and open circuit conditions (the value of  $D_0$  has been chosen to fit the experimental results).

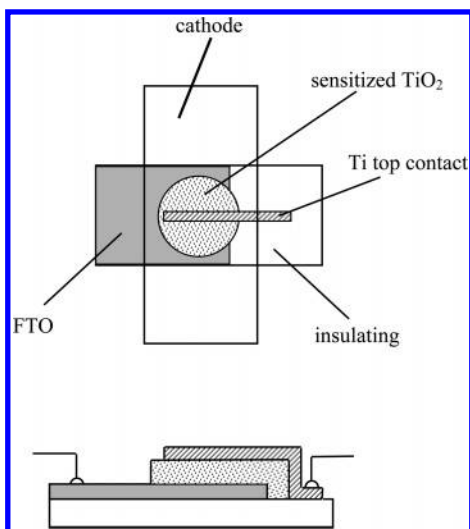
It can be seen from Figure 1 that the QFL at  $x = d$  remains at a high value relative to the redox Fermi level, even when the cell is short circuited, pinning the Fermi level to  $E_{F,redox}$  at  $x = 0$ . By contrast, under open circuit conditions, the QFL is the same at  $x = 0$  and  $x = d$ . The figure also shows how the difference in the QFL between the substrate and electrolyte sides of the film is expected to decrease along the  $IV$  characteristic toward open circuit.

## Experimental Section

Ideally, the electron QFL should be measured with respect to the equilibrium redox potential, but in practice, the electron QFL at  $x = d$  relative to the Fermi level of the redox system is more conveniently measured with respect to the potential of the DSC cathode. Under short circuit conditions at 1 sun, the potential of the cathode can deviate from that of the reversible  $\text{I}_3^-/\text{I}^-$  couple as a consequence of the kinetic and mass transport contributions to the cathode overvoltage, which depends on current density. However, in the case of platinum-coated cathodes, the overvoltage should be small (typically less than  $5 \text{ mV}^{13}$ ), so that the platinum electrode remains close to the equilibrium redox Fermi level.

To isolate the internal titanium electrode from the FTO-coated glass substrate (TEC 15 Pilkington USA), the working electrodes were masked off using polyimide tape and the exposed areas were removed by repeated etching using zinc granules covered by a few drops of concentrated HCl. The etched substrates were cleaned before application of a thin blocking layer of  $\text{TiO}_2$  by spray pyrolysis as described elsewhere.<sup>14</sup> The  $\text{TiO}_2$  colloid was spread by doctor blading using a circular Scotch tape mask to give a 5 mm diameter disk of  $\text{TiO}_2$  on the conducting substrate with a very small (1 mm) overlap with the insulating etched region of the FTO substrate to prevent shorting, as shown in Figure 3. The cell design was optimized to minimize errors arising from the part of the  $\text{TiO}_2$  layer on the insulating substrate. If the area of the uncontacted part is too large, photogenerated electrons may flow from the uncontacted area to the contacted area via the titanium secondary electrode, giving rise to an error in the measured QFL.

The nanocrystalline  $\text{TiO}_2$  layers were heated in air for 25 min at  $450^\circ\text{C}$  using a hot air gun to give porous anatase films about  $4\text{--}6 \mu\text{m}$  thick. Film thickness values were measured using a Dektak 6 M profilometer. The film was sensitized with N719, and the cell was filled with the electrolyte, which consisted of



**Figure 3.** Schematic diagrams (top view and side view) showing the cell construction used to measure the quasi-Fermi level on the top side of the nanocrystalline  $\text{TiO}_2$  layer via a passivated titanium electrode (the cathode is not shown in the side view).

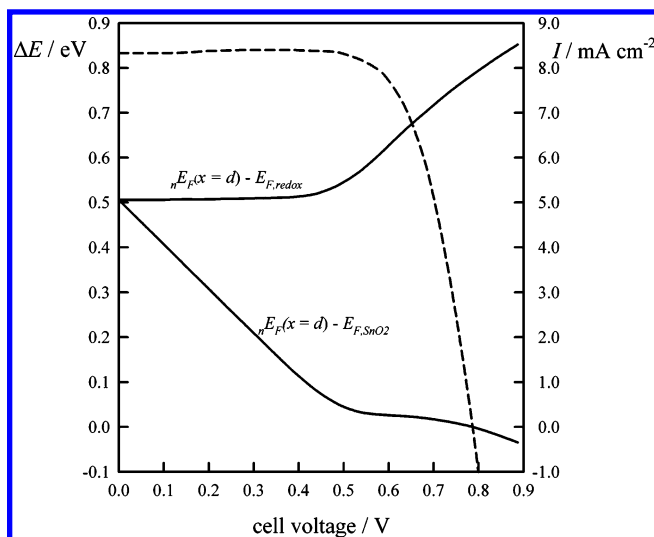
0.1 M Li and 0.05M  $\text{I}_2$  in acetonitrile containing 0.5 M tertiary butyl pyridine.

The titanium electrode contact at the top of the  $\text{TiO}_2$  porous layer was prepared by thermal evaporation through a mask to give a 1 mm wide strip with a thickness of around 100 nm. To measure reliable values of the QFL, it is essential that the secondary electrode does not provide an additional route for back reaction of electrons with  $\text{I}_3^-$  ions, because this will alter the QFL profile across the nanocrystalline film. Open circuit decay measurements that will be described elsewhere<sup>14</sup> showed that the thin natural oxide film on the titanium electrode does not completely suppress electron transfer, so further thermal oxidation in air was performed at 450 °C for 10 min to yield a thicker passivating oxide layer. This thickness strongly inhibits back electron transfer to  $\text{I}_3^-$  but allows equilibration with the QFL in the nanocrystalline  $\text{TiO}_2$ .

*IV* characteristics were measured using a calibrated AM1.5 solar simulator at 1 sun. Measurements with the secondary electrode were made using monochromatic illumination (535 nm) at intensities adjusted to give short circuit currents corresponding to 1 sun. Monochromatic radiation was used in order to be able to use a defined value of  $\alpha$  in the fitting. The value of  $\alpha$  used in the fitting was calculated from the photocurrent and the film thickness. The potential of the titanium internal electrode was measured with respect to both the platinum-coated cathode and the conducting glass anode using a high impedance voltage follower.

## Results and Discussion

Figure 4 illustrates how the QFL values measured at the titanium secondary electrode relative to the cathode and the anode contacts vary as the DSC is scanned along the *IV* characteristic at an illumination intensity corresponding to 1.0 sun. It can be seen that the predicted behavior is reproduced by the experimental results. The data obtained at 1 sun show that under short circuit conditions the electron QFL lies 0.51 eV above the redox Fermi level. The key variables that determine this value are the diffusion coefficient of conduction band electrons,  $D_0$ , the conduction band density of states,  $N_C$ , and the energy separation between the conduction band and the redox Fermi level,  $E_C - E_{F,\text{redox}}$ . The value of the electron lifetime,  $\tau_0$ , is unimportant under short circuit conditions



**Figure 4.** Experimental *IV* characteristic and corresponding variation of the quasi-Fermi level at  $x = d$  relative to the redox Fermi level,  $E_{F,\text{redox}}$ , and relative to the Fermi level in the tin oxide substrate,  $E_{F,\text{SnO}_2}$ . The experimental results should be compared with the theoretical plots shown in Figure 1.

provided that the electron diffusion length exceeds the film thickness, which is the case for the cells studied here. However, the value  $\tau_0$  is important in determining the open circuit voltage. A good fit to the experimental value of the electron QFL at  $x = d$  as well as to the experimental *IV* characteristics was obtained for  $D_0 = 0.4 \text{ cm}^2 \text{ s}^{-1}$  (the value for bulk anatase),  $N_C = 10^{21} \text{ cm}^{-3}$ ,  $E_C - E_{F,\text{redox}} = 0.95 \text{ eV}$ , and  $\tau_0 = 10^{-2} \text{ s}$ . Several measurements suggest that  $D_0$  is considerably lower in nanocrystalline  $\text{TiO}_2$  compared with bulk anatase.<sup>16,17</sup> However, fitting of the QFL using lower values of  $D_0$  requires smaller values of  $E_C - E_{F,\text{redox}}$  and correspondingly longer lifetimes that are greater than those measured by photovoltage decay and intensity modulated photovoltage spectroscopy. For example, if  $D_0$  is reduced by 1 order of magnitude,  $E_C - E_{F,\text{redox}}$  must be reduced by 59 meV and  $\tau_0$  must be increased by an order of magnitude to obtain a fit. Similarly, changes are required if  $N_C$  is decreased by an order of magnitude. Independent measurement of some of these quantities is necessary in order to refine the values further.

## Conclusions

The profile of the electron QFL in the DSC can be conveniently probed using a passivated titanium electrode. The results confirm the existence of a large difference (0.5 eV) in the free energy of electrons across the film under short circuit conditions. Cells with a titanium secondary electrode have also been used to provide information about the behavior of the electron QFL as a function of temperature.<sup>15</sup>

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