

# Direct Measurement of the Temperature Coefficient of the Electron Quasi-Fermi Level in Dye-Sensitized Nanocrystalline Solar Cells Using a Titanium Sensor Electrode

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A novel type of dye-sensitized cell (DSC) with a passivated titanium sensor electrode located on top of the nanocrystalline titanium dioxide layer has been used to study the temperature dependence of the electron quasi-Fermi level relative to the  $I_3^-/I^-$  redox-Fermi level under short circuit conditions. The results show that the Fermi level decreases with increasing temperature ( $-1.76 \text{ meV K}^{-1}$ ) as predicted for diffusive electron transport at short circuit. A smaller temperature dependence ( $-0.25 \text{ meV K}^{-1}$ ) of the position of the  $\text{TiO}_2$  conduction band relative to the  $I_3^-/I^-$  redox-Fermi level was deduced from the shifts in the trap distribution. An expression for the temperature dependence of the open circuit voltage,  $U_{\text{photo}}$ , has been derived. The experimentally observed temperature dependence of  $U_{\text{photo}}$  gave values of the activation energy (0.25 eV) and preexponential factor ( $10^8 \text{ s}^{-1}$ ) for the transfer of electrons from the conduction band of the nanocrystalline  $\text{TiO}_2$  to triiodide ions.

## Introduction

Electron transport in dye-sensitized solar cells (DSC) has been the topic of extensive discussion. The first quantitative treatment appears to have been given by Södergren et al.,<sup>1</sup> who assumed that the bulk of the nanocrystalline  $\text{TiO}_2$  film is field-free so that electron transport occurs by diffusion. These authors showed that solution of the generation collection problem (the continuity equation) for stationary conditions gives an expression that is formally identical to the diode equation for a p–n junction, although the physical processes in the DSC are quite different. Later time-<sup>2</sup> and frequency-<sup>3–5</sup>resolved studies of the photocurrent response showed that the diffusion of electrons in the DSC appears to be a continuous time random walk process<sup>6</sup> retarded by multiple trapping at states located in the band gap of the  $\text{TiO}_2$ .<sup>7</sup> However, the validity of the multiple trapping controlled diffusion model has been questioned on the basis of the results of measurements that give values of the activation energy for electron transport that are lower than expected.<sup>8–10</sup> However, we have argued recently that measurements of the electron transit time made under short circuit conditions do not give true values of the activation energy for electron diffusion because the electron quasi-Fermi level changes with temperature in such a way as to maintain constant electron flux in the bulk of the film.<sup>11</sup> In the present work we provide direct experimental proof that the electron quasi-Fermi level (QFL) does indeed fall with increasing temperature in the way predicted for diffusion-controlled electron collection. A passivated titanium indicator electrode deposited on the electrolyte side of the nanocrystalline  $\text{TiO}_2$  film has been used to measure the local QFL relative to the redox-Fermi level as a function of temperature. In addition, the temperature dependence of the conduction band position was estimated from shifts in the voltage dependence of the trapped electron charge,<sup>10</sup> and the temperature dependence of the open circuit voltage has been considered theoretically and measured experimentally. The theoretical treatment yields the perhaps surprising result that the temperature coefficient of  $U_{\text{photo}}$  is independent of the activation energy for

the back reaction but depends on the light intensity and the preexponential factor for the recombination reaction.

## Experimental Section

Details of the fabrication of cells including a passivated titanium indicator electrode have been reported previously.<sup>12</sup> The cells were mounted on a Peltier thermostat and illuminated with a solid-state laser at 532 nm at an intensity that gave the same current density ( $10.2 \text{ mA cm}^{-2}$ ) as illumination with a solar simulator (AM 1.5 1 sun). The stored charge in the cell was evaluated as a function of photovoltage and temperature using the charge extraction technique described elsewhere.<sup>13–15</sup>

## Theory

We assume that injection and collection of electrons in the DSC can be described by the continuity equation

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

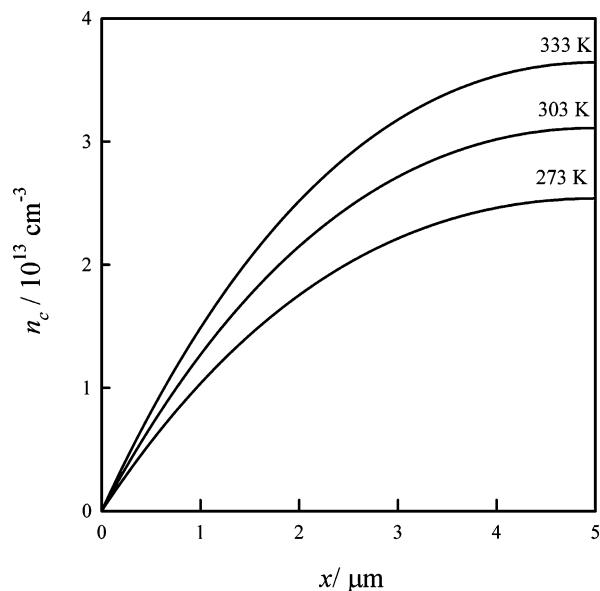
Here  $n_c(x)$  is the position-dependent density of conduction band electrons,  $n_{\text{eq}}$  is the density of conduction band electrons when the system is in equilibrium in the dark (i.e., the Fermi level in the oxide is equal to the redox-Fermi level  $E_{\text{F,redox}}$ ),  $\alpha$  is the absorption coefficient of the sensitized layer,  $I_0$  is the incident photon flux corrected for reflection losses,  $D_0$  is the diffusion coefficient of electrons in the conduction band, and  $k_0$ , the pseudo-first-order rate constant for the transfer of electrons from the conduction band to redox species (usually  $I_3^-$ ), is the reciprocal of the conduction band electron lifetime,  $\tau_0$  (electron transfer via surface states has been neglected for simplicity).

For illumination from the anode side ( $x = 0$ ), the boundary conditions are

$$\frac{dn_c}{dx} \Big|_{x=0} = 0 \text{ and } n_c(0+) \rightarrow n_{\text{eq}} \exp(qU/k_B T) \quad (2)$$

(it is assumed that electron extraction at the anode is fast).

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**Figure 1.** Profiles of conduction band electron density  $n_c(x)$  under short circuit conditions calculated from eq 1 for three different temperatures. Values used in the calculation:  $d = 5 \mu\text{m}$ ,  $I_0 = 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$ ,  $\alpha = 2000 \text{ cm}^{-1}$ ,  $D_0 (298 \text{ K}) = 0.4 \text{ cm}^2 \text{ s}^{-1}$ ,  $N_c (298 \text{ K}) = 10^{21} \text{ cm}^{-3}$ ,  $E_c - E_{F,\text{redox}} = 0.98 \text{ eV}$ ,  $\tau_0 = 10^{-4} \text{ s}$ . The increase in  $n_c$  with temperature arises from the decrease in  $D_0$ .

Solution of eq 1 under short conditions gives the profile of conduction band electrons,  $n_c(x)$ , and hence the electron quasi-Fermi level,  ${}_nE_F$ , relative to the conduction band<sup>11</sup> since

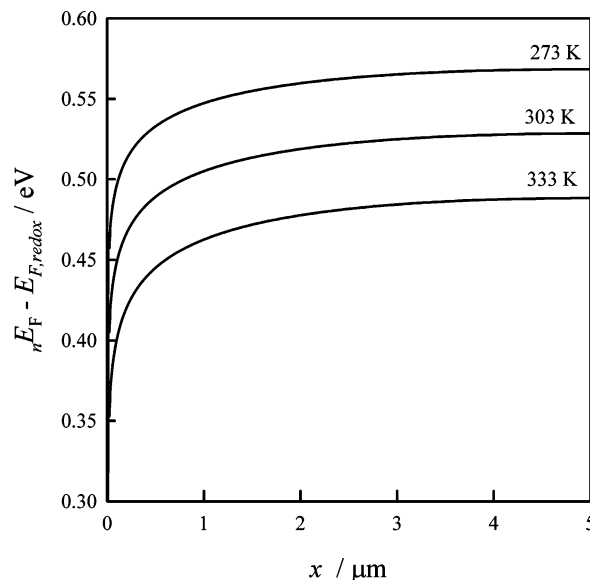
$$n_c = N_c \exp(-(E_c - {}_nE_F/k_B T)) \quad (3)$$

Provided that the collection of photoinjected electrons is complete (i.e., the electron diffusion length is greater than the thickness of the  $\text{TiO}_2$  film), the influence of temperature under short circuit conditions is expected to be restricted to changes in the conduction band density of states (proportional to  $T^{3/2}$ ) and changes in the mobility of electrons in the  $\text{TiO}_2$  conduction band.<sup>11,16</sup> Forro et al.<sup>16</sup> have reported that for  $T > 160 \text{ K}$ , the mobility,  $\mu_0$ , of electrons in anatase single crystals decreases with temperature in proportion to  $\exp(T_0/T)$ , with  $T_0 = 850 \text{ K}$ . It follows from the Einstein relationship ( $D_0 = (k_B T/q)\mu_0$ ) that  $D_0$  should vary with  $T \exp(T_0/T)$ . For single-crystal anatase, the Hall mobility measurement reported by Forro et al. corresponds to a room-temperature value of  $D_0 \approx 0.4 \text{ cm}^2 \text{ s}^{-1}$ . The temperature-dependent conduction band electron density profiles calculated from eq 1 are shown in Figure 1.

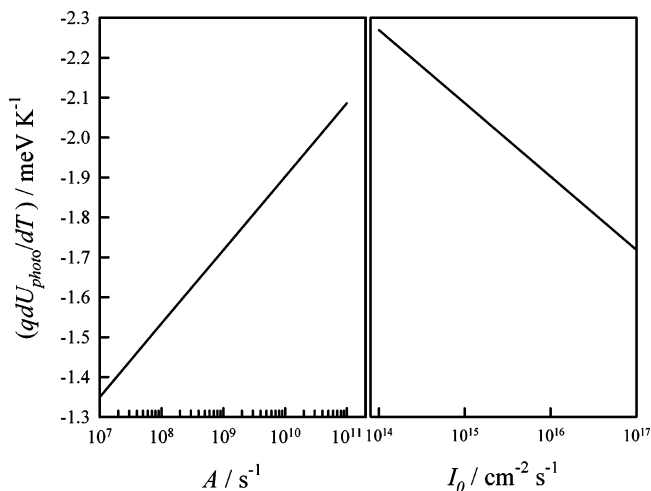
It can be seen that the decrease in electron diffusion coefficient with increasing temperature should lead to an increase in the electron density in order to sustain the (constant) photocurrent (see ref 11 for a discussion of this point). The lowering of the electron quasi-Fermi level profiles with temperature shown in Figure 2 follows from eq 3, noting that the conduction band density of states  $N_c$  increases proportional to  $T^{3/2}$ .

It is worth noting at this point that the effects of temperature on the QFL arising from decreasing the electron diffusion coefficient  $D_0$  and increasing  $N_c$  are of opposite sign and both are second-order effects, so that the change in QFL can be approximated quite well by the linear expression<sup>11</sup>

$$E_c - {}_nE_{F,T_2}(x) = \left(\frac{T_2}{T_1}\right)(E_c - {}_nE_{F,T_1}(x)) \quad (4)$$



**Figure 2.** Profiles of the electron quasi-Fermi level  ${}_nE_F$  relative to the redox-Fermi level  $E_{F,\text{redox}}$  calculated using the same values as in Figure 1. Note that the model predicts that the electron quasi-Fermi level should decrease with temperature.



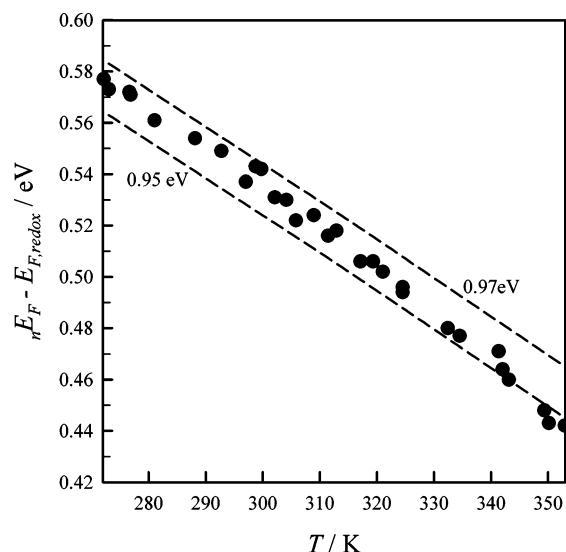
**Figure 3.** Predicted dependence of the temperature coefficient of the open circuit voltage  $U_{\text{photo}}$  on the preexponential factor for electron back reaction ( $A$ ) and on the light intensity ( $I_0$ ).  $E_c - E_{F,\text{redox}} (298 \text{ K}) = 0.98 \text{ eV}$  (the calculation assumes that  $E_c - E_{F,\text{redox}}$  is constant). The left-hand plot is for  $I_0 = 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$  and variable  $A$ . The right-hand plot is for  $A = 10^9 \text{ s}^{-1}$  and variable  $I_0$ .

The position of the electron QFL under open circuit conditions is also readily derived by noting that the conduction band electron density under photostationary conditions is determined by the balance between photoinjection and back reaction. The conduction band electron density ( $n_c \gg n_{\text{eq}}$ ) under open circuit conditions is given to a good approximation by

$$n_c = \frac{I_{\text{abs}}}{k_0 d} = \frac{I_0(1 - e^{-\alpha d})}{k_0 d} \quad (5)$$

where  $I_{\text{abs}}$  is the absorbed photon flux and  $d$  is the film thickness. The temperature dependence of the rate constant  $k_0$  for the reaction of conduction band electrons with  $\text{I}_3^-$  can be written as

$$k_0 = A \exp(-\epsilon_A/k_B T) \quad (6)$$



**Figure 4.** Experimental variation of the electron quasi-Fermi level relative to the redox-Fermi level measure using the titanium electrode (open circles). The lines are calculated for the same values as in Figure 1, except that the  $E_c - E_{F,\text{redox}}$  was varied as shown. The experimental data can be fitted exactly if it is assumed that  $E_c - E_{F,\text{redox}}$  decreases with temperature with a coefficient of  $-0.25 \text{ meV K}^{-1}$ . This value was confirmed by measuring the voltage dependence of the electron trap distributions as a function of temperature.

where  $\epsilon_A$  is the activation energy and  $A$  is the preexponential factor. Substituting eqs 5 and 6 into eq 3 gives the photovoltage as a function of temperature:

$$qU_{\text{photo}} = (E_c - E_{F,\text{redox}}) + k_B T \ln\left(\frac{I_{\text{abs}}}{d}\right) - k_B T \ln N_c - k_B T \ln A + \epsilon_A \quad (7)$$

It follows that the temperature coefficient of the photovoltage is given by

$$\frac{dU_{\text{photo}}}{dT} = k_B \ln\left(\frac{I_{\text{abs}}}{d}\right) - k_B \ln N_c - k_B \ln A \quad (8)$$

Since the temperature dependence of  $N_c$  can be written in the form

$$N_c(T) = N_{c,298} \left(\frac{T}{298}\right)^{3/2} \quad (9)$$

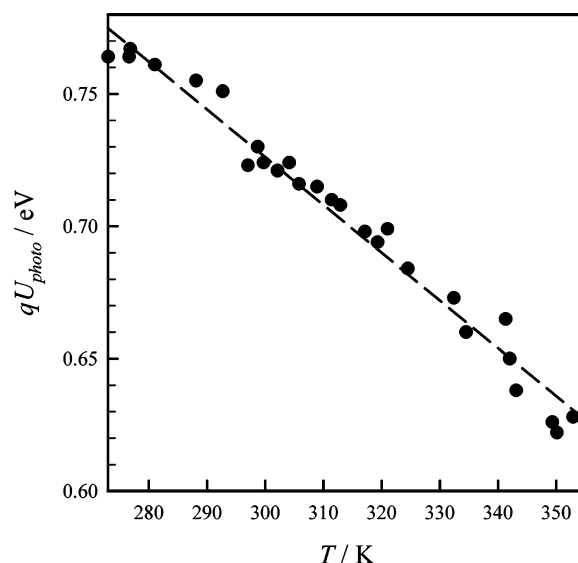
we obtain

$$\frac{dU_{\text{photo}}}{dT} = k_B \ln\left(\frac{I_{\text{abs}}}{d}\right) - k_B \ln N_{c,298} + \frac{3}{2} k_B \ln\left(\frac{T}{298}\right) + \frac{3}{2} k_B - k_B \ln A \quad (10)$$

It can be seen from eq 10 that the temperature dependence of the open circuit voltage is independent of  $\epsilon_a$ , but depends on light intensity  $I_0$  and on the preexponential factor  $A$  as illustrated in Figure 3.

## Results and Discussion

The experimentally observed variation of the electron QFL at  $x = d$  measured under short circuit conditions at 1 sun using the titanium electrode is shown in Figure 4 together with variations calculated from the continuity equation for different values of the energy of the conduction band relative to the redox Fermi level (the calculation takes into account the temperature



**Figure 5.** Experimental temperature dependence of the open circuit voltage  $U_{\text{photo}}$  and the best linear fit obtained from eq 7 using the following values.  $I_0 = 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$ ,  $d = 5 \text{ }\mu\text{m}$ ,  $\alpha = 2000 \text{ cm}^{-1}$ ,  $N_c(298 \text{ K}) = 10^{21} \text{ cm}^{-3}$ ,  $E_c - E_{F,\text{redox}}(298 \text{ K}) = 0.98 \text{ eV}$ ,  $A = 10^8 \text{ s}^{-1}$  and  $\epsilon_a = 0.25 \text{ eV}$ . The calculation takes the temperature dependences of  $N_c$  and of  $E_c - E_{F,\text{redox}}$  into account (coefficient  $-0.25 \text{ eV K}^{-1}$ ). The low value of the preexponential factor is attributed to the triiodide iodine preequilibrium (see text).

dependence of  $D_0$  and  $N_c$ ). It can be seen that the slope of the experimental plot is slightly higher than the slope of the lines calculated for constant  $E_c - E_{F,\text{redox}}$ . O'Regan and Durrant<sup>17</sup> have reported that this energy difference is temperature dependent with a coefficient of  $-1.7 \text{ meV K}^{-1}$ . However, the deviation from the calculated lines evident in Figure 4 suggests a significantly smaller variation of  $E_c - E_{F,\text{redox}}$  of  $-0.25 \text{ meV K}^{-1}$ . This value was confirmed by using the charge extraction technique<sup>13</sup> to measure the stored charge in the cell as a function of photovoltage ( $nE_F - E_{F,\text{redox}}$ ) for different temperatures. The observed small displacements of the charge curves along the voltage axis confirmed that the temperature coefficient of  $E_c - E_{F,\text{redox}}$  in our cells is only  $-0.3 \pm 0.1 \text{ meV K}^{-1}$ . This agrees very well with the small additional dependence required to obtain a good fit to the temperature dependence of the electron QFL at  $x = d$  shown in Figure 4.

The temperature dependence of the open circuit voltage of the cell was also measured, and the results are presented in Figure 5. The figure also shows the best linear fit using eq 7 (cf. Figure 3). The slope of the line was fitted by varying the preexponential factor  $A$ , and the absolute magnitude of the voltage was fitted by varying the activation energy  $\epsilon_a$ . The calculation assumed that the density of states in the conduction band at 298 K is  $10^{21} \text{ cm}^{-3}$  and  $E_c - E_{F,\text{redox}} = 0.98 \text{ eV}$  at 298 K. The values obtained from the linear fit are  $A = 10^8 \text{ s}^{-1}$  and  $\epsilon_a = 0.25 \text{ eV}$ , corresponding to a conduction band electron lifetime at 293 K of  $\tau_0 = 2 \times 10^{-4} \text{ s}$ . The value of  $A$  obtained depends linearly on the value chosen for  $N_c$ : the fit for  $N_{c,298} = 10^{20} \text{ cm}^{-3}$  gives a value of  $A = 10^9 \text{ s}^{-1}$  and a correspondingly shorter conduction band lifetime of  $2 \times 10^{-5} \text{ s}$ .

If, as an approximation, we consider the back reaction as a second-order homogeneous process, then the first-order preexponential factor  $A$  is related to the second-order preexponential factor  $A_2$  by

$$A = A_2[I_3^-] \quad (11)$$

where  $[I_3^-]$  is the volume density of triiodide ions. If the

preexponential factor is estimated from the conventional expression for diffusion controlled homogeneous collision rate between two species, noting that the diffusion coefficient of electrons is much higher than that of triiodide ions, we obtain  $A_2 [I_3^-] \approx 10^{13} \text{ s}^{-1}$ . The much lower values ( $10^8$ – $10^9 \text{ s}^{-1}$ ) obtained from the fit suggest that the reacting species is not  $I_3^-$  but instead  $I_2$ , which is present in much lower concentration as a consequence of the high value of the association constant for the  $I_2 + I^- \rightleftharpoons I_3^-$  equilibrium<sup>5,18</sup> ( $\approx 10^7 \text{ mol dm}^{-3}$ ).

## Conclusions

Taken together with independent evidence for high densities of trapped electrons in dye sensitized nanocrystalline solar cells, the observed decrease of the electron quasi-Fermi level with increasing temperature under short circuit conditions provides direct experimental proof of the validity of the theoretical model for electron transport. The observed temperature dependence of the open circuit voltage is also consistent with the theoretical treatment, which shows that the temperature coefficient of the open circuit voltage is independent of the activation energy for the back reaction but dependent on the conduction band density of states and the preexponential factor for electron transfer.

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