

# Determination of the Density and Energetic Distribution of Electron Traps in Dye-Sensitized Nanocrystalline Solar Cells

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Electron transport and recombination in dye-sensitized nanocrystalline solar cells (DSCs) are strongly influenced by the presence of trapping states in the titanium dioxide particles, and collection of photoinjected electrons at the contact can require times ranging from milliseconds to seconds, depending on the illumination intensity. A direct method of determining the density and energetic distribution of the trapping states responsible for slowing electron transport has been developed. It involves extraction of trapped electrons by switching the cell from an open circuit to a short circuit after a period of illumination. An advantage of this charge extraction method is that it is less sensitive than other methods to shunting of the DSC by electron transfer at the conducting glass substrate. Results derived from charge extraction measurements on DSCs (with and without compact TiO<sub>2</sub> blocking layers) are compared with those obtained by analysis of the open circuit photovoltage decay.

## Introduction

Electron transport in dye-sensitized nanocrystalline solar cells is remarkably slow, with typical collection times for photoinjected electrons ranging from tens of milliseconds at one sun intensity to tens of seconds at low light intensity.<sup>1–3</sup> Electron transport to the anode involves slow percolation through a network of interconnected titanium dioxide nanoparticles permeated by a redox electrolyte or other “hole-conducting” medium. Clearly, interfacial electron transfer across the high surface area of the nanocrystalline network must also be slow to prevent loss of the photoinjected electrons during transit to the anode. This is evidently the case, since efficient cells can be fabricated (at the time of writing, the record AM 1.5 efficiency stands at 11%).<sup>4</sup> It appears that the processes that slow electron transport also retard the rate of electron loss by transfer to the redox electrolyte or hole-conducting medium. As a consequence, the apparent electron lifetime,  $\tau_n$ , is comparable with the mean transit time for electron collection. Both  $\tau_n$  and the apparent electron diffusion coefficient,  $D_n$ , depend on illumination intensity. The former decreases with intensity, whereas the latter increases. This compensation effect leads to an electron diffusion length,  $L_n = (D_n\tau_n)^{1/2}$ , that is essentially independent of light intensity.<sup>2</sup>

Kopidakis et al.<sup>5</sup> have suggested that the rate of interfacial electron transfer is limited by the rate at which electrons can reach the surface of the TiO<sub>2</sub> particles, which could explain the compensation effect. On the other hand, Bisquert et al.<sup>6,7</sup> have demonstrated that the compensation effect could arise from the existence of a quasi-static balance between free and trapped electrons in the nanocrystalline oxide. The assumption of a quasi-static balance simplifies the theoretical treatment, allowing information about trap densities and distributions to be derived from the open circuit photovoltage decay.<sup>8,9</sup> However, we have demonstrated recently that such analyses can be subject to significant errors arising from electron transfer to I<sub>3</sub><sup>−</sup> ions at

the conducting glass substrate. This process provides an additional route for the decay of the electron concentration in the nanocrystalline oxide.<sup>10–12</sup> In the present paper, we describe how the density and energetic distribution of electron traps can be measured directly by extracting the trapped charge, even under conditions where the back-reaction occurs at the substrate. This is done by short circuiting the cell at some point on the photovoltage curve and integrating the current arising from the transfer of electrons from traps in the TiO<sub>2</sub> to the anode (charge extraction).<sup>13</sup>

Dye-sensitized cells fabricated with and without blocking layers of compact TiO<sub>2</sub> were studied. It was concluded that the charge extraction method provides useful information about electron traps in *both* types of cells. In contrast, analysis of the photovoltage decay data from cells without blocking layers may lead to erroneous conclusions about the density and energetic distribution of electron traps.<sup>12</sup>

## Theory

**Determination of the Density of States Function for Electron Traps from Photovoltage Decay.** The quasi-static condition formulated by Bisquert and Vikhrenko<sup>7</sup> relates the time dependence of the conduction band electron density,  $\partial n_c / \partial t$ , in the nanocrystalline oxide to the corresponding rate of change of the density of trapped electrons,  $\partial n_t / \partial t$ .

$$\frac{\partial n_t}{\partial t} = \frac{\partial n_t}{\partial n_c} \frac{\partial n_c}{\partial t} \quad (1)$$

The photovoltage is related to the ratio of the conduction band electron densities in the dark ( $n_{c,\text{dark}}$ ) and under illumination ( $n_c$ ) by

$$\frac{n_c}{n_{c,\text{dark}}} = e^{qU_{\text{photo}}/k_B T} \quad (2)$$

where  $n_{c,\text{dark}}$  is determined by the difference between the TiO<sub>2</sub>

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conduction band energy  $E_c$  and the redox Fermi level  $E_{F,\text{redox}}$ .

$$n_{c,\text{dark}} = N_c e^{-(E_c - E_{F,\text{redox}})/k_B T} \quad (3)$$

Here  $N_c$  is the effective density of the conduction band states.

The relaxation time constant for electrons in the conduction band is often referred to as the electron lifetime or apparent electron lifetime, but it is important to recognize that it is determined not only by the rate of loss of electrons in the back-reaction but also by changes in electron trap occupancy. For  $\partial n_t / \partial n_c \gg 1$ , the relaxation time constant can be defined as

$$\tau_n = \left( \frac{\partial n_t}{\partial n_c} \right) \frac{1}{k_{cb}} = \left( \frac{\partial n_t}{\partial n_c} \right) \tau_0 \quad (4)$$

where  $k_{cb}$  is the first-order rate constant for the reaction of electrons in the conduction band with the oxidized redox species in the electrolyte.<sup>21</sup> It has been shown that  $\tau_n$  is related to the slope of the photovoltage decay curve by<sup>7,8</sup>

$$\tau_n = - \frac{k_B T}{q} \left( \frac{dU_{\text{photo}}}{dt} \right)^{-1} \quad (5)$$

In general, the derivative  $\partial n_t / \partial n_c$  is related to any density of states function for electron traps  $s_t(E)$  by

$$\frac{\partial n_t}{\partial n_c} = \frac{k_B T}{n_c} s_t(E) \quad (6)$$

It follows that the density of states function  $s_t(nE_F - E_{F,\text{redox}})$ , where  $nE_F$  is the electron quasi-Fermi level (QFL), can be obtained from the electron relaxation time constant  $\tau_n$  measured as a function of the photovoltage

$$s_t(nE_F - E_{F,\text{redox}}) = s_t(qU_{\text{photo}}) = k_{cb} \tau_n \frac{n_c}{k_B T} = k_{cb} \tau_n \frac{N_c}{k_B T} e^{-[(E_c - E_{F,\text{redox}}) + qU_{\text{photo}}]/k_B T} \quad (7)$$

provided that the values of  $k_{cb}$ ,  $N_c$ , and  $(E_c - E_{F,\text{redox}})$  are known a priori.

**Direct Measurement of the Density and Distribution of Trapped Electrons by Charge Extraction.** In principle, the charge extraction technique gives direct access to the density of trapped electrons over the energy interval  $E_{F,\text{redox}}$  to  $(E_{F,\text{redox}} + qU_{\text{photo}})$ , so that  $s_t(qU_{\text{photo}})$  can be obtained by differentiation of the number density of extracted electrons with respect to the photovoltages at which the cell is short circuited during the photovoltage decay. No a priori assumptions are required. Comparison of the direct (charge extraction) and indirect (photovoltage decay method) approaches should therefore allow reasonable bounds to be set for  $(E_c - E_{F,\text{redox}})$  if  $k_{cb}$  is known.

Efficient collection of trapped electrons can only occur if the electron diffusion length is greater than the thickness of the nanocrystalline film.<sup>2</sup> Bisquert and Vkhrenko<sup>7</sup> have argued convincingly that the diffusion length is independent of trap occupancy since the effects of trapping on the electron diffusion coefficient and electron lifetime compensate each other, so that

$$L_n = \sqrt{D_n \tau_n} = \sqrt{D_0 \tau_0} \quad (8)$$

Here,  $D_0$  is the diffusion coefficient of conduction band electrons and  $\tau_0 = 1/k_{cb}$ . Bisquert and Vkhrenko<sup>7</sup> refer to  $D_n$  as the “chemical diffusion coefficient” for electrons, i.e., the apparent diffusion coefficient resulting from multiple trapping. In the limit  $\partial n_t / \partial n_c \gg 1$ ,  $D_n$  is given by

$$D_n = \left( \frac{\partial n_c}{\partial n_t} \right) D_0 \quad (9)$$

$\tau_n$ , the relaxation time of conduction band electrons associated with trapping and the back-reaction, is given in the limit  $\partial n_t / \partial n_c \gg 1$  by

$$\tau_n = \left( \frac{\partial n_t}{\partial n_c} \right) \tau_0 \quad (10)$$

These limiting expressions lead to the constant value of  $L_n$  in eq 8.

**Time Constants Associated with Relaxation of Free and Trapped Electrons.** The time constants for the decay of the free and trapped electrons are related by eq 1. Whereas photovoltage methods measure the decay of free electrons, the charge extraction method can be used to determine the rate at which the total (i.e., predominantly trapped) electron density decays. If the density of states function for the electron traps follows an exponential energy dependence of the form<sup>22</sup>

$$s_t(nE_F - E_{F,\text{redox}}) = s_t(0) e^{[\beta(nE_F - E_{F,\text{redox}})]/k_B T} = s_t(0) e^{[\beta q U_{\text{photo}}]/k_B T} \quad (11)$$

(where  $s_t(0)$  is the density of states function at the dark Fermi level  $E_{F,\text{redox}}$  and  $\beta$  is a parameter describing the broadening of the energetic distribution of traps), it is easy to show from eq 1 that the relaxation time for the loss of trapped electrons,  $\tau_{\text{trap}}$ , is related to  $\tau_n$  by

$$\frac{\tau_{\text{trap}}}{\tau_n} = \beta \quad (12)$$

It follows that methods based on the transient or periodic photovoltage response (i.e., photovoltage decay<sup>14</sup> and intensity modulated photovoltage spectroscopy (IMVS)<sup>15,16</sup>) are not expected to give the same time constant as methods based on measuring the trapped electron charge (charge extraction<sup>13,17</sup> and light-modulated infrared absorption<sup>18</sup>).

**Efficiency of Charge Extraction.** In the charge extraction technique, the trapped charge is obtained by integration of the short circuit current in the dark. The release of trapped electrons becomes slower as the electron quasi-Fermi level falls, setting a lower limit for accurate measurement. The transit time for electrons across the entire film (thickness  $d$ ) is given by

$$t_n = \frac{d^2}{D_n} \quad (13)$$

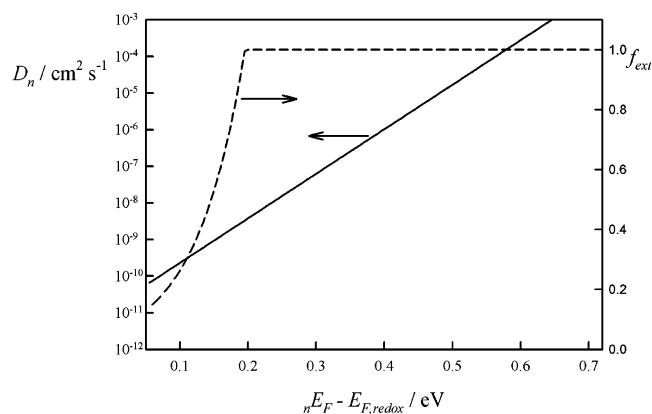
Here,  $D_n$  decreases as the quasi-Fermi level falls. In the case where the energy distribution of density of trapping states is exponential (cf. eq 11),  $D_n$  is given by<sup>7</sup>

$$D_n = \frac{N_c^\beta}{\beta N_t} n_c^{1-\beta} D_0 \quad (14)$$

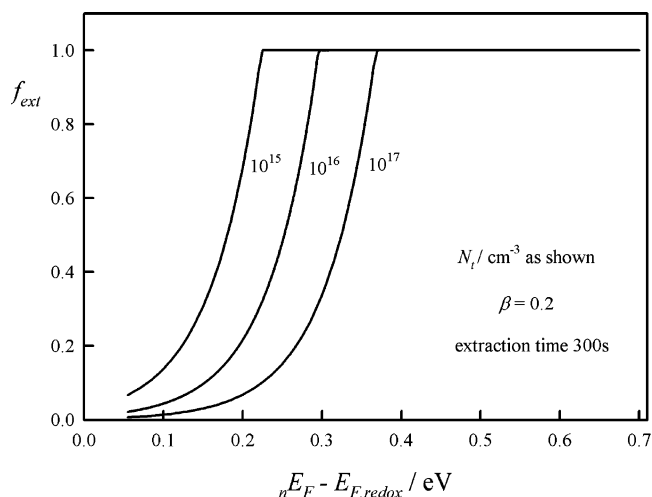
where  $N_t$  is the total trap density. The density of conduction band electrons,  $n_c$ , is given by

$$n_c = N_c e^{-(E_c - nE_F)/k_B T} \quad (15)$$

It follows that the fraction of electrons extracted in a given period will in general depend on the value of  $D_n$  and the film thickness. The fraction of electrons ( $f_{\text{ext}}$ ) extracted in a given



**Figure 1.** Dependence of the effective electron diffusion coefficient  $D_n$  on the electron quasi-Fermi level relative to the dark Fermi level calculated using eq 14. Note that the difference ( $nE_F - E_{F,redox}$ ) is equivalent to  $qU_{photo}$ . The figure also shows  $f_{ext}$ , the fraction of electrons that will be extracted in 300 s when the cell is short circuited at a given point on the photovoltage decay curve. See the Appendix for values used in these calculations.



**Figure 2.** Dependence of the fraction of charge extracted ( $f_{ext}$ ) on the total trap density calculated using eq 16. The values of  $N_t$  and  $\beta$  are shown. See the Appendix for other values used in the calculations.

extraction period ( $t_{ext}$ ) from traps in a small interval around  $nE_F$  can be defined as

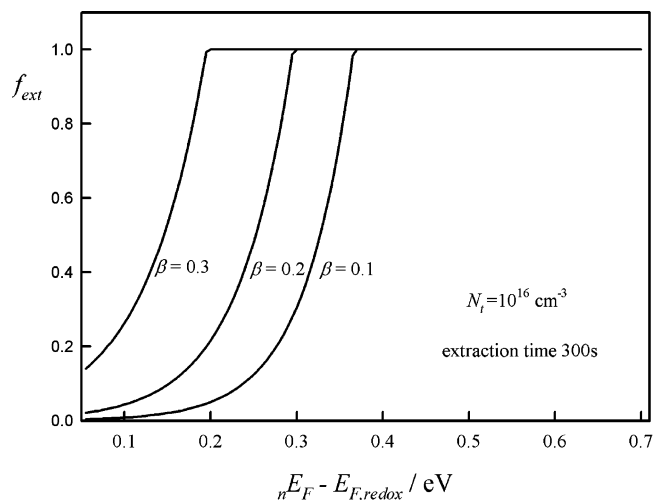
$$f_{ext} = \frac{\sqrt{t_{ext} D_n}}{d} \quad (16)$$

where  $D_n$  is given by eq 13.

Figure 1 illustrates the result of a typical calculation based on eqs 13 and 16 for an exponential trap distribution with  $N_t = 10^{15} \text{ cm}^{-3}$ ,  $\beta = 0.2$ ,  $d = 10 \text{ } \mu\text{m}$ , and  $t_{ext} = 300 \text{ s}$ . The power law dependence of  $D_n$  on the position of the electron QFL relative to the redox Fermi level is evident from the semilogarithmic plot. It can be seen that all electrons should be collected until the QFL has fallen to 0.2 eV above the redox Fermi level. At this point, the transit time begins to exceed the extraction time, so only electrons close to the contact are collected.

The fraction of electrons extracted depends on the total trap density,  $N_t$ , and the  $\beta$  parameter in the density of states distribution function defined in eq 11. Figures 2 and 3 illustrate how these parameters influence  $f_{ext}$ .

**Sources of Error in the Charge Extraction Method.** The preceding analysis suggests that reliable data should be obtained provided that the electron diffusion length is greater than the



**Figure 3.** Dependence of the fraction of charge extracted on  $\beta$  calculated using eq 16. The values of  $N_t$  and  $\beta$  are shown. See the Appendix for other values used in the calculations.

film thickness and the transit time is shorter than the integration period. However, not all of the collected charge will originate from the nanocrystalline layer. The capacitance of the interface between the conducting glass substrate and the electrolyte will be charged by the photovoltage, and this charge will also be measured when the cell is short circuited.

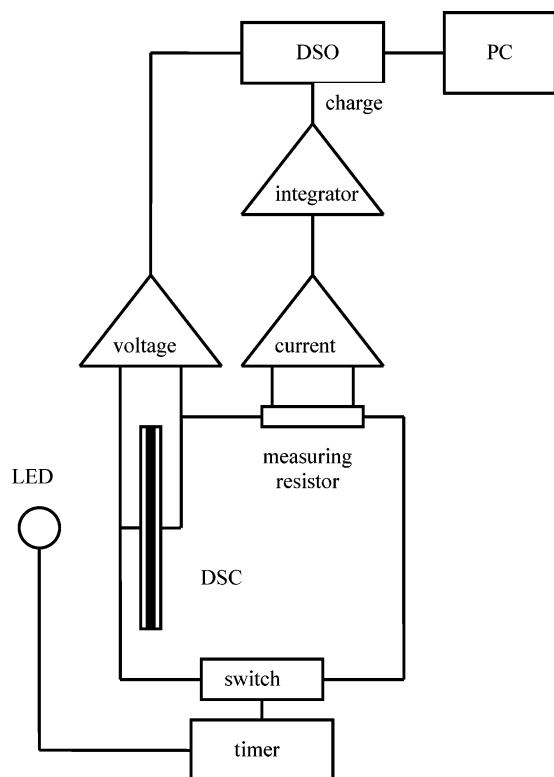
The charge stored in the interface at any value of the photovoltage is given by

$$Q_{int} = \int_{U_{dark}}^{U_{dark} + U_{photo}} C(U) dU \quad (17)$$

where  $C(U)$  is the potential dependent capacitance, which can usually be described by the Mott–Schottky equation. The fluorine-doped tin oxide coating used for conducting glass substrates is highly doped, and the interfacial capacitance is correspondingly high—typically several microfarads per square centimeter. In the case of cells with a blocking layer of compact  $\text{TiO}_2$  to prevent the back-reaction at the substrate, the space charge capacitance is considerably smaller,<sup>10</sup> reducing the error due to charge storage at the interface. Nevertheless, it should be noted that uncertainties in the correction will affect the resolution of the method, particularly for thinner nanocrystalline  $\text{TiO}_2$  films or low trap densities. In the present work, a correction to  $Q_{ext}$  was applied using values of the interfacial capacitance measured for both bare and blocked substrates as a function of the potential relative to the equilibrium  $\text{I}_3^-/\text{I}^-$  potential (see Experimental Section as well as ref 10 for details).

## Experimental Section

Dye-sensitized solar cells were prepared with and without  $\text{TiO}_2$  blocking underlayers. Blocking layers were prepared as described previously.<sup>10</sup> The thickness of the blocking layer was on the order of 100 nm. Aqueous nanocrystalline  $\text{TiO}_2$  colloid was made by the acetic acid hydrolysis route described elsewhere.<sup>19</sup> The colloid was coated onto the prepared FTO by the doctor-blading technique using adhesive tape spacers. The nanocrystalline films were fired in a stream of hot air at 450 °C for 30 min and then placed overnight in a dye bath consisting of 1.5 mM *cis*-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis-tetrabutylammonium (N719) in a 50/50 acetonitrile/*tert*-butyl alcohol mixture while still warm. The dyed films were removed, rinsed in acetonitrile, and dried in a stream of nitrogen before being sealed to a platinized counter

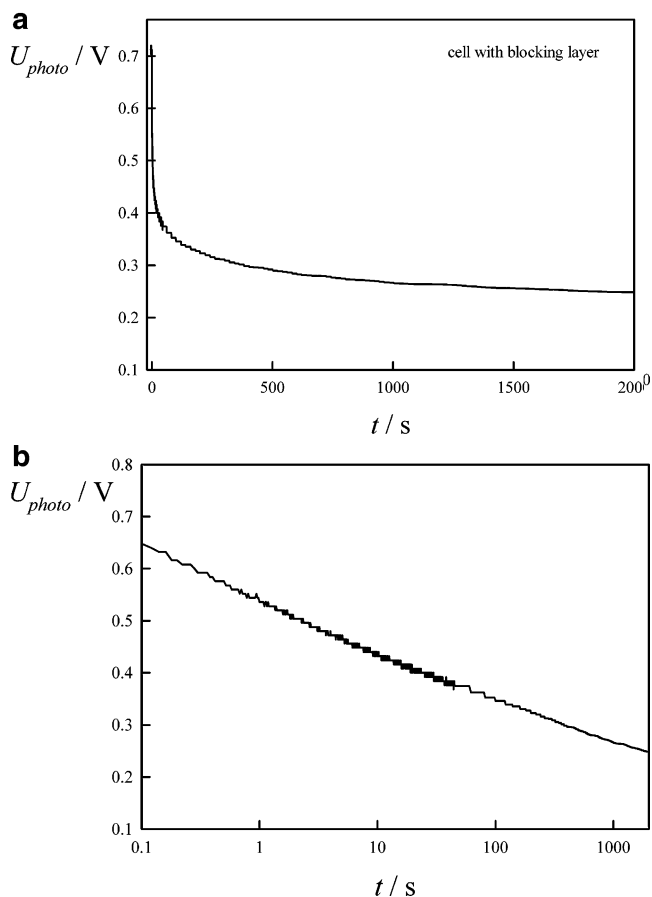


**Figure 4.** Schematic diagram of the apparatus used in the charge extraction measurements. DSO indicates the digital storage oscilloscope controlled by a PC.

electrode. Finally, the cells were filled with the redox electrolyte, which consisted of 0.85 M methylhexylimidazolium iodide, 0.1 M LiI (anhydrous 99.999%, Aldrich), 0.05 M  $I_2$  (anhydrous 99.999%, Aldrich), and 0.2 M *tert*-butylpyridine (99%, Aldrich) in acetonitrile. The thickness of the nanocrystalline layers was determined by profilometry to be in the range 13–17  $\mu\text{m}$ . The IV characteristics of cells with blocking layers were found to be superior to those of cells prepared using clean bare FTO (better open circuit photovoltage and higher fill factor).

The characterization of bare and blocked substrates by electrochemical impedance spectroscopy has been described previously.<sup>10</sup> The capacitance of the highly doped bare electrode over the range of the photovoltage decay is on the order of 5  $\mu\text{F cm}^{-2}$ , whereas the capacitance of the blocked electrodes is lower (in this case 1  $\mu\text{F cm}^{-2}$ ) as a consequence of the lower doping density of the  $\text{TiO}_2$  layer (typically  $10^{18} \text{ cm}^{-3}$ ). The measured capacitance values were used to correct the charge extraction data. In the case of the bare electrode, the correction amounted to 30% of the total charge, whereas, in the case of the cell with the blocking layer, the correction was less than 10%.

Photovoltage decay and charge extraction measurements were made using a purpose-built instrument developed from a setup described earlier.<sup>13</sup> The system (shown schematically in Figure 4) allows the cell to be illuminated under open circuit conditions with a light-emitting diode for a specified time, after which the photovoltage decay is recorded for a further period before the cell is short circuited through a measuring resistor by means of a fast relay switch. The current observed when the cell is short circuited across the measurement resistor is due to the collection of electrons still remaining in the nanocrystalline oxide film after the photovoltage has been allowed to decay for a certain time. This current transient is integrated using a low drift (chopper stabilized) integrator to obtain the trapped charge.



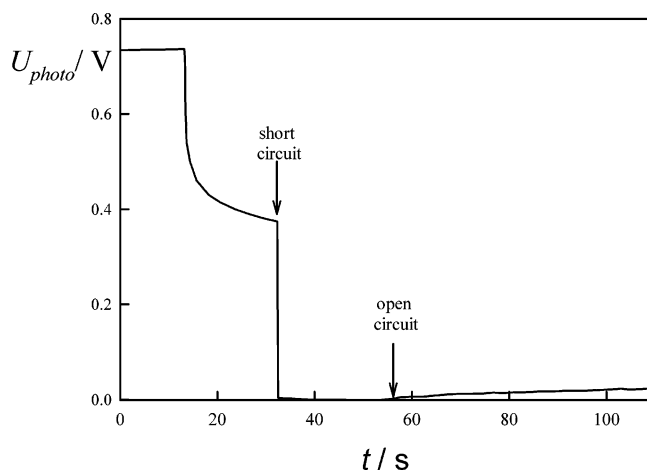
**Figure 5.** (a) Example of the extraordinarily slow photovoltage decay seen for cells with a thin compact blocking layer of  $\text{TiO}_2$  to limit the back-reaction at the substrate. (b) Semilogarithmic plot showing that the photovoltage decay depends on  $\log t$ , as expected for an exponential distribution of electron traps.

Voltage and charge transients were recorded using a digital oscilloscope and transferred to a PC for data treatment. The quantity of trapped charge was determined as a function of the photovoltage by repeating the measurements with different decay periods determined by the timer. The density of states function for electron traps was then obtained by numerical differentiation after appropriate corrections for the contribution of substrate charging were made.

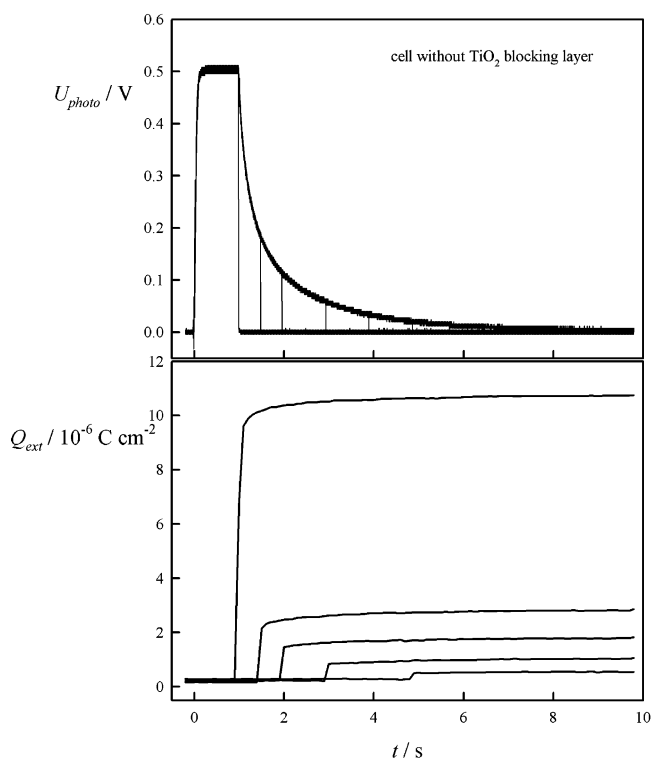
## Results and Discussion

Our previous work<sup>12</sup> has shown that the photovoltage decay of DSCs is very slow when a thin blocking layer of  $\text{TiO}_2$  is used to inhibit the back-reaction of electrons with  $I_3^-$  at the FTO substrate. An example of the extraordinarily slow decay that was observed for a number of different cells with blocking layers is shown in Figure 5a (a voltage amplifier with an input impedance of greater than  $10^{12} \Omega$  was used to measure this decay). Figure 5b shows that the photovoltage decay follows the logarithmic dependence on time characteristic of an exponential distribution of trapping states for at least 1000 s. In contrast, DSCs with bare clean FTO substrates generally exhibit much more rapid photovoltage decays. The apparent values of  $\tau_{\text{nf}}$  or the two types of cells derived using eq 5 have been discussed previously.<sup>12</sup>

Figure 6 shows an example of the photovoltage transient measured using the same cell during the charge extraction measurement. In this particular case, the cell was short circuited for 20 s and then switched to open circuit gain. Only a small



**Figure 6.** Illustration of the effect of short circuiting the cell for 20 s. Note that only a small residual photovoltage is observed when the cell is returned to an open circuit state. This indicates that most of the trapped carriers are extracted in 20 s.

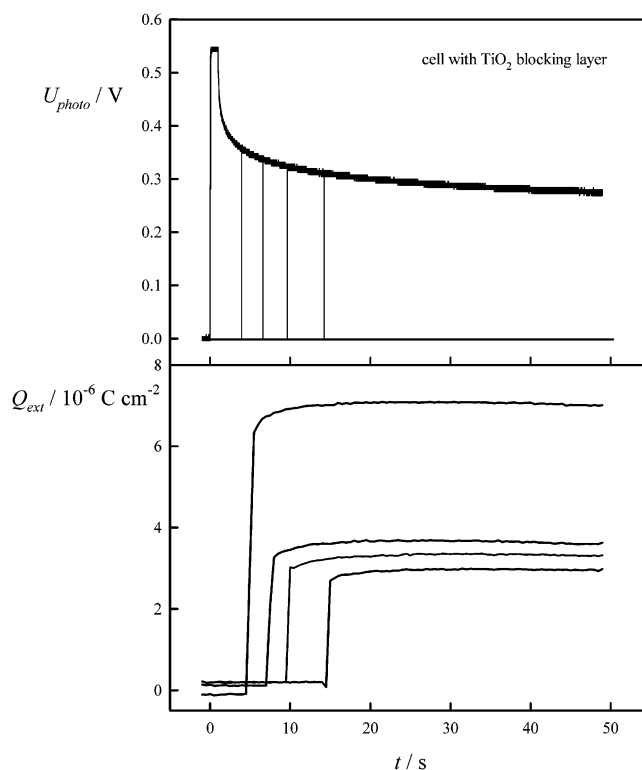


**Figure 7.** Set of photovoltage decay transients and the corresponding charge extraction transients measured for different delay periods for a cell with no blocking layer. Note the rapid decay of the photovoltage and the corresponding decrease in extracted charge.

residual photovoltage was observed, indicating that charge extraction under short circuit conditions has removed virtually all of the electrons in the cell.<sup>23</sup>

Figures 7 and 8 illustrate the difference between cells with and without blocking layers (measured at low illumination intensity to reduce thermal effects). The figures also show that the stored charge decays more rapidly for the cell without a blocking layer.

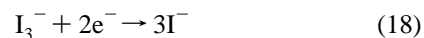
In the case of the cell without a blocking layer, derivation of the density of states function for electron traps from the photovoltage decay will clearly lead to spurious results.<sup>12</sup> This raises the interesting question of whether analysis of the charge extraction data for this cell is similarly flawed. The charge extraction method requires only that the collection efficiency



**Figure 8.** Set of photovoltage decay transients and the corresponding charge extraction transients measured for different delay periods for a cell with a compact TiO<sub>2</sub> blocking layer. Note the much slower decay of the photovoltage and the correspondingly higher extracted charges (compare to Figure 5).

for electron collection approaches unity under short circuit conditions. The back-reaction at the substrate is unimportant in this context, since the driving force for this process is negligibly small for a short circuit state. This contrasts with the situation during open circuit photovoltage decay, where the driving force for the transfer of electrons to I<sub>3</sub><sup>−</sup> is determined by the photovoltage. We conclude, therefore, that the charge extraction technique can provide reliable results, even if a blocking layer is absent. In fact, the more rapid decay is quite convenient, since it allows ready access to lower photovoltages on a reasonable time scale.

In our previous work using the charge extraction method,<sup>19</sup> we analyzed the time dependence of the total electron density in an attempt to establish the reaction order of the net reaction

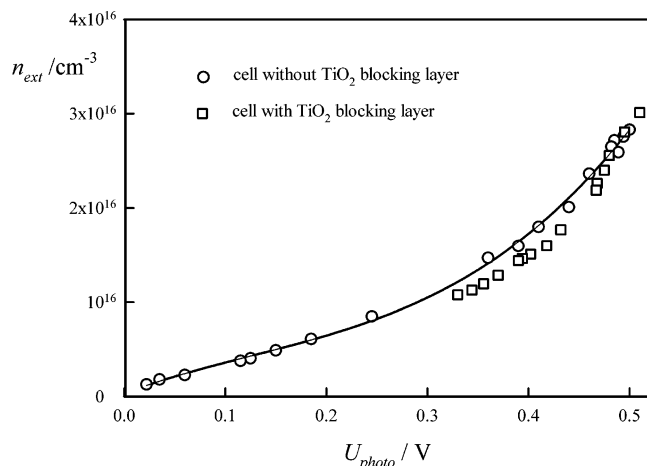


with respect to the electron concentration. However, this analysis is suspect, since the cells used in the study did not have a blocking layer to inhibit reaction 18 from occurring at the substrate. Here, we examine the relationship between the total trapped electron density measured by charge extraction ( $n_{\text{ext}}$ ) and the photovoltage. In principle, the trapped electron density is given by the integral

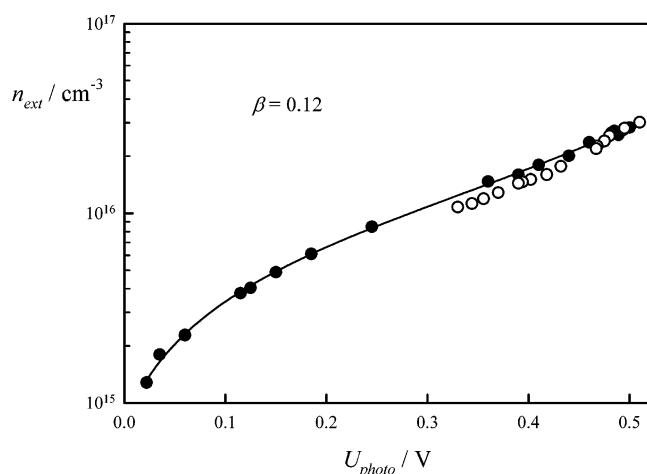
$$n_{\text{ext}} = \frac{Q_{\text{ext}}}{qd} = \int_{nE_{\text{F,redox}}}^{nE_{\text{F,redox}} + qU_{\text{photo}}} s(E) dE \quad (19)$$

so that the density of states function can be found by taking the derivative of  $n_{\text{ext}}$  with respect to the photovoltage value at which the charge extraction is performed. However, before calculating the value of  $n_{\text{ext}}$ , it is necessary to make a correction for the charge on the substrate. This was done in the present





**Figure 9.** Plot of extracted electron densities (corrected for interface charging) for cells with and without blocking layers as a function of the photovoltage at which charge extraction was performed.



**Figure 10.** Semilogarithmic plot of the extracted charge density for a cell with no blocking layer (filled circles) and a cell with a blocking layer (open circles). The line shows the data fit to an exponential distribution (cf. eq 11) of electron traps with  $\beta = 0.12$  and  $s_t(0) = 3 \times 10^{15} \text{ cm}^{-3} \text{ eV}^{-1}$ .

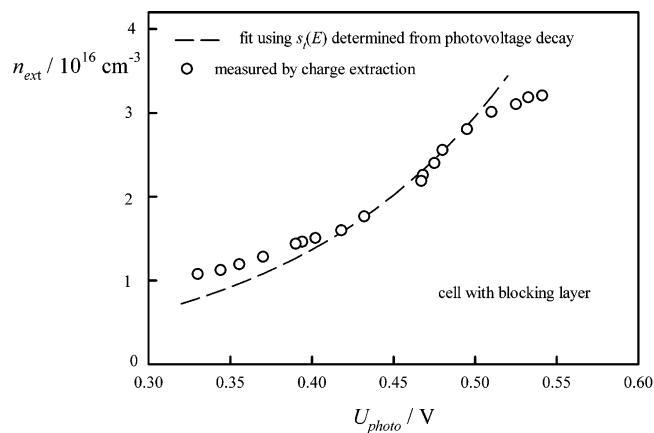
case using values of the interfacial capacitance measured for the bare and coated FTO electrodes.

Figure 9 compares the results for the two cells. It can be seen that the charge density in the two cases is very similar. The data for the cell without a blocking layer extend to low values of photovoltage because the photovoltage decay is more rapid as a consequence of the back-reaction at the FTO substrate. The line shows the least-squares fit of the extracted electron density data to an exponential density of states function (eq 11) with  $s_t(0) = 2.8 \times 10^{15} \text{ cm}^{-3} \text{ eV}^{-1}$  and  $\beta = 0.12$ . Figure 10 illustrates the density of states function  $s_t(0)$  derived from the data for both of the cells. It can be seen that both sets of data are similar, except that the values for the cell with no blocking layer extend to lower photovoltages, as expected.

The function  $s_t(0)$  is related to the total density of traps  $N_t$  by

$$s_t(0) = \frac{\beta N_t}{k_B T} e^{\beta(E_{F,\text{redox}} - E_c)/k_B T} \quad (20)$$

so that  $N_t$  can be determined if  $(E_c - E_{F,\text{redox}})$  is known. An estimate of the value of this energy difference was made by noting the fact that the data for the cell without a blocking layer



**Figure 11.** Comparison of the charge extraction and photovoltage decay methods for a cell with a blocking layer. The plot compares the experimentally measured values of extracted charge (corrected for interface charging) with the best fit curve calculated using the value of  $\beta$  determined by analyzing the photovoltage decay. The comparison gives the position of the conduction band of the  $\text{TiO}_2$  relative to the redox Fermi level as 0.95 eV. See the text for further details.

follow the exponential distribution down to low photovoltages. This suggests that electrons can still be extracted when the photovoltage has fallen to 0.1 V, placing a lower bound on the value of the electron diffusion coefficient  $D_n$  of around  $10^{-7} \text{ cm}^2 \text{ s}^{-1}$  at this photovoltage. Savenije et al.<sup>20</sup> have measured the mobilities of free electrons in compact and nanocrystalline anatase films using time-resolved microwave conductivity measurements and have obtained values from 0.3 to  $1.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The corresponding values of the free electron diffusion coefficient are in the range  $(0.8\text{--}5.0) \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ . In previous measurements, we established that the electron diffusion length exceeded the film thickness for  $10 \mu\text{m}$  cells. This is consistent with the high IPCEs observed. It follows that  $D_{n,0}\tau_{n,0} \geq 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . For  $D_n = 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ , this corresponds to  $\tau_{n,0} \geq 10^{-4} \text{ s}$ .<sup>24</sup> A free electron lifetime of  $10^{-4} \text{ s}$  was, therefore, used in the expression for the density of states function derived previously to give the following:<sup>12</sup>

$$s_t(qU_{\text{photo}}) = \left( \frac{\tau_n}{\tau_{n,0}} \right) \left( \frac{n_{c,0}}{k_B T} \right) \exp\left( \frac{qU_{\text{photo}}}{k_B T} \right) = \left( \frac{\tau_n}{\tau_{n,0}} \right) \left( \frac{N_c}{k_B T} \right) \exp\left( \frac{-(E_c - E_F + qU_{\text{photo}})}{k_B T} \right) \quad (21)$$

Integration of this expression gives the extracted electron density for any photovoltage provided that  $\tau_{n,0}$ ,  $N_c$ , and  $(E_c - E_{F,\text{redox}})$  are known. Using  $\tau_{n,0} = 10^{-4} \text{ s}$  and  $N_c = 10^{21} \text{ cm}^{-3}$  allows us to estimate  $(E_c - E_{F,\text{redox}})$  by fitting the integrated form of eq 21 to the extracted electron density measured experimentally. Figure 10 illustrates the comparison.

The fit gives  $(E_c - E_{F,\text{redox}}) = 0.95 \text{ V}$ , which is consistent with estimates made by Bisquert et al.<sup>14</sup> However, the fit in Figure 11 is clearly not perfect. This reflects the fact that the  $\beta$  value obtained by the charge extraction method (0.12) is smaller than that which was derived from the photovoltage decay (0.19). However, in view of uncertainties associated with correction for double layer charging, the difference may not be significant.

The uncertainty in  $\beta$  gives rise to a substantial uncertainty in  $N_t$ . Using  $\beta = 0.12$  and  $(E_c - E_{F,\text{redox}}) = 0.95 \text{ V}$ ,  $s_t(0) = 3 \times 10^{15} \text{ cm}^{-3} \text{ eV}^{-1}$  gives a total density of traps,  $N_t = 6 \times 10^{16} \text{ cm}^{-3}$ , corresponding to approximately 1–2 traps per  $\text{TiO}_2$  particle. Using a higher value of  $\beta = 0.16$  and the same value

of  $s_t(0)$  gives  $N_t = 2.6 \times 10^{17} \text{ cm}^{-3}$ , corresponding to around 4–8 traps per particle.

It is worth noting that the photovoltage decay method and the charge extraction method both become unreliable for deep states (low photovoltages). In the case of the photovoltage decay method, this is due to the influence of the back-reaction at the substrate. In the case of the charge extraction method, this is due to the fact that not all carriers will be extracted on the time scale of the measurement.

## Conclusions

The present study has shown that the density of trapped electrons can be determined as a function of the electron quasi-Fermi level without the need to make any additional assumptions. The charge extraction method is, therefore, particularly useful for cells where shunting occurs at the substrate, preventing reliable analysis of photovoltage decay transients. Further work is in progress to relate information about electron trapping to factors such as  $\text{TiO}_2$  colloid preparation routes and surface treatments.

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## Appendix

The following values were used in calculations (Figures 1–3):  $N_c = 10^{21} \text{ cm}^{-3}$ ;  $(E_c - E_{F,\text{redox}}) = 1.0 \text{ eV}$ ;  $k_{cb} = 10^{-4} \text{ s}^{-1}$ ;  $D_{n,0} = 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ ;  $d = 10^{-3} \text{ cm}$ ;  $k_{cb} = 10^4 \text{ s}^{-1}$ ;  $T = 298 \text{ K}$ .

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- (21) It is assumed that the reaction of conduction band electrons with  $\text{I}_3^-$  is first order with respect to the electron concentration. See ref 11 for a discussion of this assumption.
- (22) An alternative way of defining the distribution is  $g_t(E) = \beta N_t / k_B T \exp[\beta(E - E_c)/k_B T]$ . This is equivalent to eq 11 with  $s_t(0) = \beta N_t / k_B T \exp[\beta(E_{F,\text{redox}} - E_c)/k_B T]$ . Here  $N_t$  is the total trap density.
- (23) We thank one of the reviewers for suggesting this experiment.
- (24) In a recent paper,<sup>12</sup> we used a lower value of  $10^{-6} \text{ s}$  in theoretical calculations, but the argument given here suggests that this value is too small.