

## Recombination and Transport Processes in Dye-Sensitized Solar Cells Investigated under Working Conditions

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The transport and recombination of electrons in dye-sensitized TiO<sub>2</sub> solar cells were studied by analysis of the current and voltage response to a small square-wave light-intensity modulation. Solar cells were studied under working conditions by using potentiostatic and galvanostatic conditions. An increase in applied voltage, that is, from 0 V toward open-circuit voltage, was found to lead to *faster* electron transport at low light intensities, while it *slowed* transport at higher light intensities. This observation seems to be conflicting with the multiple trapping model with diffusive transport. An effective diffusion length at the maximum power point was calculated, and it was shown that it decreases with increasing light intensity.

### Introduction

Dye-sensitized solar cells (DSCs) based on nanocrystalline TiO<sub>2</sub> electrodes exhibit high power conversion efficiency and have the potential for low-cost production.<sup>1–3</sup> In the porous TiO<sub>2</sub> film of the DSC, the electron transport process competes with charge recombination to oxidized dye molecules and electron accepting species in the electrolyte. To obtain efficient solar cells, electron transport must dominate over recombination processes under actual working conditions, that is, conditions where the solar cell delivers current as well as voltage.

Electron transport in dye-sensitized nanostructured TiO<sub>2</sub> has mainly been studied under short-circuit (SC) conditions as a function of light intensity. A power-law dependence between transport time and light intensity has been found.<sup>4–10</sup> The effect of applied potential was considered in only a few studies.<sup>11,12</sup> Diffusion is considered to be the main driving force for electron transport through the porous TiO<sub>2</sub> film<sup>13</sup> for the following reasons: First, the nanoparticles are not doped and are too small to contain significant band bending. Second, electrons in the nanostructure are effectively screened by ions in the surrounding electrolyte. No significant macroscopic electrical fields are therefore expected in the porous film.

Recombination of electrons to oxidized dye molecules has been studied as a function of light intensity and applied potential.<sup>14</sup> In actual solar cells, this recombination reaction is expected to play a limited role, as the regeneration reaction of the oxidized dye with iodide is rapid. Recombination with electron accepting species in the electrolyte (i.e., triiodide) is considered to be the main recombination pathway and will be the only one considered here. While most of the studies were performed under open-circuit (OC) conditions when studying this reaction,<sup>6,8–10,15–17</sup> some have also used working conditions.<sup>12,18</sup>

The light-intensity dependence of electron transport and recombination in dye-sensitized solar cells can be explained

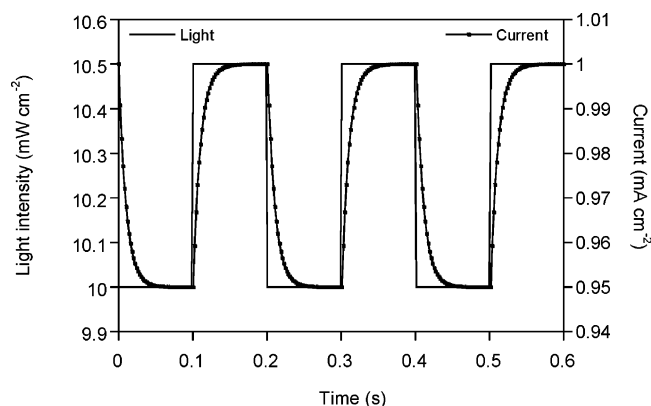
using a multiple trapping (MT) model. In this model, electrons are considered to be mostly trapped in localized states below the conduction band, from which they can escape by thermal activation. Experiments suggest that the density and energetic location of such traps is described by an exponentially decreasing tail of states below the conduction band.<sup>6,7</sup> Using a quasi-static approximation, electron transport in the MT model can be described by an effective diffusion coefficient that depends on the light intensity.<sup>19</sup>

Because of the nonlinear response of electron transport and recombination as a function of light intensity, these processes are best studied using small-modulation techniques. Frequency-resolved techniques such as intensity-modulated photocurrent and photovoltage spectroscopy have been extensively used. As these techniques are rather time-consuming, time-resolved small-modulation techniques using pulsed light<sup>18,20</sup> or square-wave modulation<sup>9,10</sup> have been developed. In this study, using the latter technique, we have studied the response of the solar cell not only under SC and OC conditions but also under working conditions, in particular at the maximum power point (MPP).

### Experimental Section

**Cell Preparation.** Nanostructured TiO<sub>2</sub> electrodes were prepared by spreading a concentrated colloidal TiO<sub>2</sub> paste onto a conducting glass substrate (TEC8, Pilkington), followed by drying and heating to 450 °C in a hot air stream for 0.5 h. Preparation of the TiO<sub>2</sub> colloidal (20 nm particle size) and paste is described elsewhere.<sup>21</sup> The resulting TiO<sub>2</sub> films (thickness 11 μm) were sensitized using *cis*-(TBA)<sub>2</sub>Ru(Hdcbpy)<sub>2</sub>(NCS)<sub>2</sub> (N719, supplied by Solaronix). Electrodes were assembled with a thermally platinized TEC8 counter electrode using a thermoplastic and filled with the electrolyte (0.6 M tetrabutylammonium iodide, 0.1 M lithium iodide, 0.05 M iodine, and 0.5 M 4-tertbutylpyridine in 3-methoxypropionitrile). The active area of the cells was 0.48 cm<sup>2</sup>.

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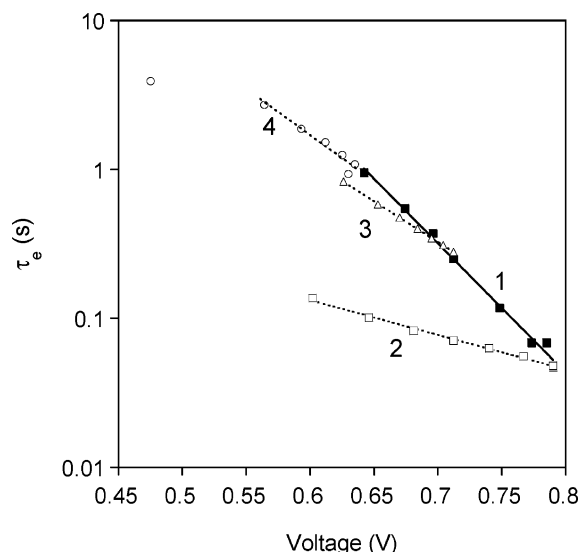
**Figure 1.** Square-wave modulation of the light intensity and the resulting photocurrent response in a dye-sensitized solar cell under potentiostatic conditions. The response is well fitted using exponential decay and rise with a time constant of 10 ms. Similar results are obtained in the galvanostatic mode, where the voltage response is measured.

**Methods.** Solar cells were connected to a potentiostat/galvanostat (EG & G Princeton Applied Research, model 273) and illuminated using red light from a light emitting diode (Luxeon Star 1W,  $\lambda_{\text{max}} = 640$  nm). The voltage or current response was digitized using a 16-bit resolution data acquisition board (National Instruments). A small square-wave modulation (<10% of intensity, 0.1–2 Hz) was added to the base light intensity. Typical solar cell response is shown in Figure 1, which is well fitted to an exponential rise or decay function. Traces were averaged 10 times in the potentiostatic mode and twice in the galvanostatic mode. Time constants and response amplitudes obtained for rise and decay were nearly equal (within 5%). The effect of RC attenuation by the substrate/electrolyte interface was found to be negligible.<sup>22</sup>

The term voltage (V) used in this work refers to the potential difference between the counter electrode and working electrode, which is either applied (potentiostatic mode) or measured (galvanostatic mode). The presented results are from a single representative solar cell.

## Results and Discussion

**Electron Lifetime as a Function of Voltage.** The measured electron lifetime ( $\tau_e$ ) is shown as a function of voltage in Figure 2. Data series 1 shows  $\tau_e$  values measured at open-circuit potential using various light intensities. An exponential relationship is found between  $\tau_e$  and  $V_{\text{OC}}$ , as reported before in several other studies.<sup>10,15,23</sup> Following a similar approach as O'Regan and Lenzmann,<sup>18</sup> a galvanostat was used to measure the electron lifetime of the DSC at a constant current. A small square-wave modulation of the light intensity on top of a much larger bias light will result in small variations of the measured voltage, as the galvanostat keeps the current constant. On a downward step in light intensity, the electron concentration will decrease. The adjustment of electron concentration occurs by recombination only as the current and the bias light are fixed. The time constant found by measuring the voltage decay is therefore the electron lifetime. Series 2–4 show  $\tau_e$  values measured under working conditions at three different light intensities. At zero current, equivalent to OC conditions, the lifetimes coincide with series 1. Under working conditions, however, the measured  $\tau_e$  value at a certain voltage is shorter than that under OC conditions and decreases with light intensity. The lifetime at 0.6 V, for example, differs by a factor of 26 between the highest and lowest light intensity ( $\tau_e = 0.1$  and 2.6 s, respectively). This observation



**Figure 2.** Electron lifetime as a function of voltage under open-circuit conditions (series 1) and under working conditions (series 2–4). Series 1 was recorded using seven light intensities in the range 0.57–28.7 mW cm<sup>-2</sup>. Series 2–4 were recorded in the galvanostatic mode at light intensities of 28.7, 2.8, and 0.57 mW cm<sup>-2</sup>, respectively. Symbols indicate measured data, and lines are exponential fits. The deviation of the exponential trend at the lowest voltage (series 4) is ascribed to recombination at the conducting glass substrate becoming dominant.<sup>23</sup>

can be explained as follows: under OC conditions, electrons are approximately uniformly distributed in the TiO<sub>2</sub> film, resulting in a constant quasi-Fermi level,  $nE_F$ . The measured voltage corresponds directly to the  $nE_F$  value of the TiO<sub>2</sub> film. Under operating conditions, however, there is a distribution in electron density and therefore a gradient in  $nE_F$  in the TiO<sub>2</sub> film. More specifically, the  $nE_F$  value of the conducting substrate, determining the measured voltage, will be lower than the average  $nE_F$  value in the TiO<sub>2</sub> film. As the measured  $\tau_e$  value is determined by the average  $nE_F$  value in the TiO<sub>2</sub> film, a smaller value for  $\tau_e$  will be found under working conditions compared to open-circuit conditions with the same voltage.

A quantitative estimation of the average quasi-Fermi level in the TiO<sub>2</sub> film can be made by correlating the lifetimes under operating and open-circuit conditions. For example, using the highest light intensity and an operating voltage of 0.60 V,  $\tau_e$  was determined to be 0.137 s (see Figure 2). This lifetime is also found at an open-circuit voltage of 0.73 V. Consequently, the average quasi-Fermi level present in the TiO<sub>2</sub> at an operating voltage of 0.60 V was 0.73 V. Similarly, one can obtain the average Fermi level under short-circuit conditions by extrapolation of the fitted  $\tau_e - V$  relation to  $V = 0$ . For the highest light intensity, a value of 0.58 V is estimated, which is close to the value measured experimentally (0.59 V).<sup>24</sup>

**Electron Transport Time as a Function of Voltage.** The photocurrent response under potentiostatic conditions was used to determine electron transport times in dye-sensitized solar cells. The measured response time ( $\tau_{\text{resp}}$ ) depends on both the electron transport time ( $\tau_{\text{tr}}$ ) and the electron lifetime. The influence of the electron lifetime can usually be neglected under short-circuit conditions. It will, however, be important when the solar cell is kept under working conditions. The following relation has been derived for the response time under potentiostatic conditions that is valid if recombination and transport are proportional to the electron concentration in TiO<sub>2</sub> and are independent processes:<sup>16</sup>

$$\frac{1}{\tau_{\text{resp}}} = \frac{1}{\tau_e} + \frac{1}{\tau_{\text{tr}}} \quad (1)$$

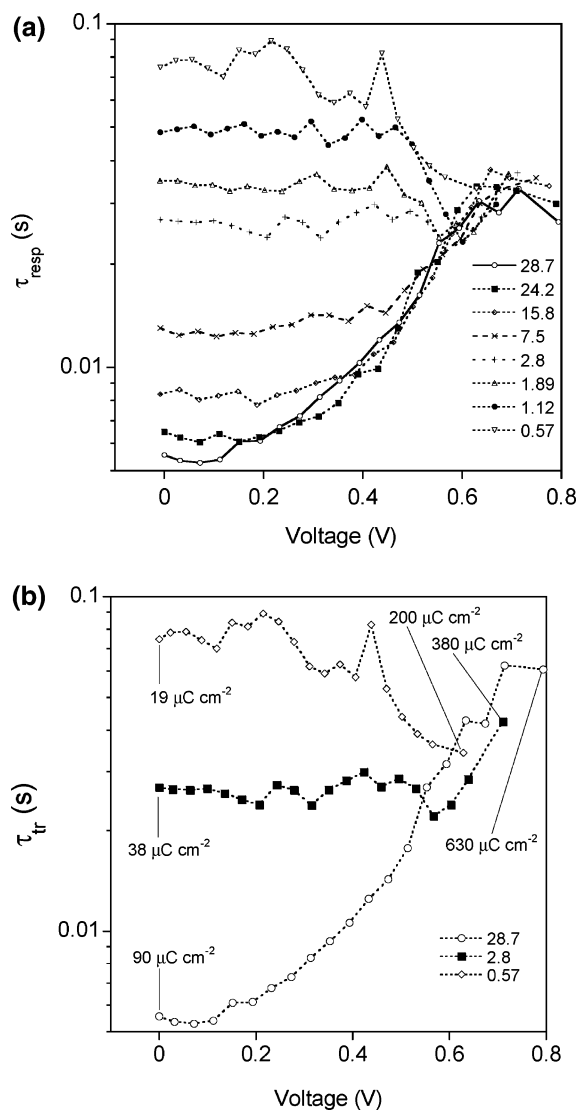
Figure 3a shows the measured photocurrent response times as a function of applied voltage at different light intensities. At low light intensities, the response time decreased with increased voltage. Intriguingly, the opposite was observed at higher light intensities. At an intermediate light intensity, the response times were almost constant over the whole voltage range. Comparison with the electron lifetime data (Figure 2) shows that the response time can be considered to be approximately equal to electron transport in most of the voltage range. Figure 3b shows the calculated transport times, using eq 1 and the data of Figures 2 and 3a for three light intensities. Only slight differences are observed at the highest voltage compared to Figure 3a. It is noted that at high voltage  $\tau_{\text{tr}}$  becomes independent of the light intensity and is solely determined by the applied voltage.

The decrease of the electron transport time with increased voltage, as observed for the lowest light intensities, can be understood with the multiple trapping model. A higher voltage leads to an increase in the quasi-Fermi level in the  $\text{TiO}_2$  film and an increased effective diffusion coefficient.<sup>19</sup> To explain the slower electron transport with increased voltage, observed at high light intensities, is more problematic. We note that a similar observation has been done by van de Lagemaat et al.,<sup>12</sup> but no explanation was given. Clearly, the observation disagrees with the multiple trapping model, that predicts faster transport when  $nE_F$  is increased.

Values of the extracted charge ( $Q$ ) under SC<sup>8</sup> and OC<sup>8,17</sup> conditions are also given in Figure 3b. Under short-circuit conditions, an increase in  $Q$  gives faster electron transport, as demonstrated before. At the lowest light intensity,  $Q$  varies from  $19 \mu\text{C cm}^{-2}$  under SC conditions to  $200 \mu\text{C cm}^{-2}$  under OC conditions. It is noted that  $\tau_{\text{tr}}$  decreases in this interval from 75 to 34 ms, but not to the value of 5.6 ms that is observed at a charge of  $90 \mu\text{C cm}^{-2}$  under SC conditions at the highest light intensity. This is another observation that is in conflict with the MT model.

The MT model that assumes electron transport by diffusion combined with multiple trapping does not seem to be able to explain the observations at high light intensities. We therefore suggest that an electric field must play a role in the electron transport in the porous  $\text{TiO}_2$ . This field can be produced by a shift of the  $\text{TiO}_2$  conduction band edge upon accumulation of electrons. A gradient in the conduction band edge level in the film may assist electron transport. Increasing the voltage lowers this gradient and will decrease the electron transport speed. An estimate on the magnitude of the conduction band shift can be made as follows: a charge of  $90 \mu\text{C cm}^{-2}$  was accumulated in the  $\text{TiO}_2$  film under SC conditions at the highest light intensity. Assuming a typical value of the Helmholtz capacitance ( $C_H$ ) of  $10^{-5} \text{ F cm}^{-2}$  for the  $\text{TiO}_2$ /electrolyte interface and considering that the roughness factor (RF) of the electrode is about 1000, an average shift of the conduction band potential in the negative direction of  $\Delta V = Q_{\text{SC}}/(C_H \times \text{RF}) = 9 \text{ mV}$  is calculated. Clearly, this is not sufficient to have a significant effect on the electron transport. The value of  $C_H$  may, however, be much smaller than that assumed in this calculation, because of the organic solvent and the adsorbed molecules at the  $\text{TiO}_2$  surface. Preliminary experiments suggest that  $C_H$  is in the order of  $10^{-6} \text{ F cm}^{-2}$ , so that significant band edge shifts can be expected.

**Electron Diffusion Length under Maximum Power Point Conditions.** The diffusion length of electrons in the dye-sensitized  $\text{TiO}_2$  film (with thickness  $w$ ) was calculated for three



**Figure 3.** (a) Photocurrent response time (potentiostatic mode) as a function of applied voltage. Eight bias light intensities in the range  $0.57\text{--}28.7 \text{ mW cm}^{-2}$  were used as indicated. (b) Electron transport times, calculated from the response time and lifetimes using eq 1, as a function of applied voltage. Extracted charge, measured under short-circuit and open-circuit conditions, is indicated in the figure, as well as the light intensities used (in  $\text{mW cm}^{-2}$ ).

light intensities. The effective electron diffusion coefficient ( $D_{\text{eff}}$ ) and the diffusion length ( $L$ ) were calculated using eqs 2<sup>20</sup> and 3, respectively.

$$D_{\text{eff}} = \frac{w^2}{2.35\tau_{\text{tr}}} \quad (2)$$

$$L = \sqrt{D_{\text{eff}}\tau_e} \quad (3)$$

Using a conventional approach,  $\tau_{\text{tr}}$  and  $\tau_e$  are measured under SC and OC conditions, respectively. The results of this approach are presented in Table 1. The calculated diffusion lengths are only weakly dependent on light intensity. This agrees well with the results of Fisher et al.,<sup>6</sup> who reported that the diffusion length of electrons in the dye-sensitized  $\text{TiO}_2$  solar cell is rather constant over several decades of light intensity, because electron transport times and lifetimes scale in opposite directions with light intensity. This observation was explained by Bisquert and Vukharenko using a quasi-static approximation of the MT

**TABLE 1: Electron Lifetime and Transport Times under Open-Circuit and Short-Circuit Conditions, Respectively, at Different Light Intensities ( $I_0$ ) and Calculated Values of the Effective Diffusion Coefficient ( $D_{\text{eff}}$ ) and the Diffusion Length ( $L$ )**

$I_0$ (mW cm <sup>-2</sup> )	$J_{\text{SC}}$ (mA cm <sup>-2</sup> )	$\tau_{\text{e,OC}}$ (s)	$\tau_{\text{tr,SC}}$ (ms)	$D_{\text{eff}}$ (m <sup>2</sup> s <sup>-1</sup> )	$L$ ( $\mu\text{m}$ )
28.7	5.0	0.048	5.6	$9.3 \times 10^{-9}$	21
2.8	0.5	0.28	27	$2.0 \times 10^{-9}$	23
0.57	0.1	0.93	75	$6.9 \times 10^{-10}$	25

**TABLE 2: Electron Lifetimes and Potentiostatic Response Times at the Maximum Power Point Voltage ( $V_{\text{MPP}}$ ) at the Three Light Intensities and Calculated Values of the Transport Time, the Effective Diffusion Coefficient ( $D_{\text{eff}}$ ), and the Diffusion Length ( $L$ )**

$I_0$ (mW cm <sup>-2</sup> )	$V_{\text{MPP}}$ (V)	$\tau_{\text{e,MPP}}$ (s)	$\tau_{\text{resp,MPP}}$ (ms)	$\tau_{\text{tr,MPP}}$ (ms)	$D_{\text{eff,MPP}}$ (m <sup>2</sup> s <sup>-1</sup> )	$L_{\text{MPP}}$ ( $\mu\text{m}$ )
28.7	0.55	0.16	23	27	$1.9 \times 10^{-9}$	18
2.8	0.60	1.2	23	24	$2.2 \times 10^{-9}$	51
0.57	0.57	2.6	36	36	$1.4 \times 10^{-9}$	61

model.<sup>19</sup> We note, however, that the  $L$  value under short-circuit conditions must be much larger than that reported, as the electron lifetime under SC conditions is much longer than that under OC conditions, by at least 1 order of magnitude (see Figure 2).

More relevant for solar cell performance is the diffusion length in the maximum power point (MPP) of the  $IV$  curve. This was calculated from  $\tau_{\text{tr}}$  and  $\tau_{\text{e}}$  measured at MPP; see Table 2.  $L$  clearly decreases with increasing light intensity. This can be attributed to a decrease in electron lifetime in the MPP with higher light intensities. Electron transport, on the other hand, is almost constant in the MPP. It is noted that  $L$  will approach the film thickness under full sun illumination. Significant losses in the solar cell efficiency may therefore be expected under actual operating conditions due to an insufficient diffusion length at the MPP.

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