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Determining the locus for photocarrier recombination in dye-sensitized solar cells

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We present intensity-modulated photocurrent and infrared transmittance measurements on dye-sensitized solar cells based on a mesoporous titania (TiO_2) matrix immersed in an iodine-based electrolyte. Under short-circuit conditions, we show that an elementary analysis accurately relates the two measurements. Under open-circuit conditions, infrared transmittance, and photovoltage measurements yield information on the characteristic depth at which electrons recombine with ions (the “locus of recombination”). For one particular series of samples recombination occurred near the substrate supporting the titania film, as opposed to homogeneously throughout the film. © 2002 American Institute of Physics. [DOI: 10.1063/1.1436533]

Dye-sensitized solar cells based on mesoporous titania (TiO_2) immersed in an iodine-based electrolyte have achieved solar conversion efficiencies of about 10% during the decade since their first successful fabrication by O'Regan and Grätzel.¹ Under short-circuit conditions, it appears that essentially every photon absorbed by a dye molecule generates a mobile electron in the porous TiO_2 which diffuses to and is collected by the conducting substrate supporting the matrix.² Open-circuit voltages are generally around 0.7 V under solar illumination. This value is much lower than what can be estimated³ from the difference (≈ 1.1 V) between the redox potential in the electrolyte and the potential of the conduction band. Understanding why the voltage is substantially lower than expected requires a comprehensive knowledge of photocarrier transport and recombination throughout the solar cell.

In this letter, we demonstrate an experimental approach to resolving a particular, smaller question, which is the macroscopic position in the cell at which recombination occurs (the “locus of recombination”). There is presently no generally accepted approach to this problem. Microscopically, under open-circuit conditions photogenerated electrons ultimately recombine by transferring to the electrolyte, which may occur at either the TiO_2 /electrolyte interface or at the substrate/electrolyte interface; the substrate is usually a transparent conducting oxide (TCO). There are two obvious models: recombination occurs fairly close to the substrate (“near-substrate recombination”) or homogeneously throughout the nanoporous titania matrix (“bulk recombination”). These two models lead to very different understanding for the open-circuit voltage. The open-circuit voltage is the difference between the “quasi-Fermi level” for electron photocarriers E_{Fe} at the substrate interface and the Fermi level of the redox system. Bulk recombination is illustrated at the left of Fig. 1, which is the commonly accepted model for dye-sensitized cells at open circuit.²⁻⁴ Note that the

quasi-Fermi level for electrons is constant throughout the TiO_2 layer. The simplicity of a flat quasi-Fermi level is lost for a near-substrate recombination model. The current of electrons flowing from the middle regions of the cell (where most photogeneration occurs) to the near-substrate region (where they recombine) leads to a quasi-Fermi level gradient,⁵ and a corresponding modification in the open-circuit voltage.

In this letter, we address the locus of recombination by comparing intensity-modulated photocurrent and photovoltage measurements in cells with the simultaneous changes in the infrared absorption. In these electrolyte-filled cells, transient photocurrents measure the arrival of photocarriers at the substrate (as opposed to displacement currents).⁶ The infrared measurements are generally thought to probe the integrated density of photocarriers throughout the cell.⁷ The photovoltage measures the quasi-Fermi level of electrons at the substrate interface.³ We use the differing spatial and temporal sensitivities of the methods to investigate the locus of recom-

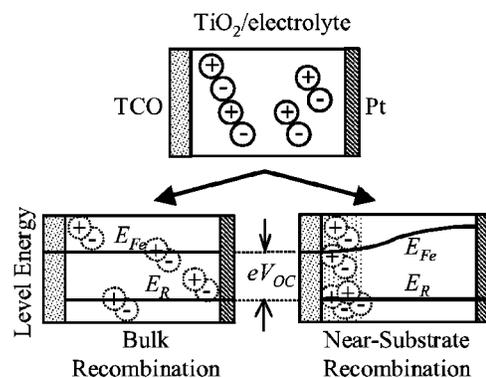


FIG. 1. Two models for photocarrier recombination in dye-sensitized solar cells under open-circuit conditions. The top panel illustrates uniform generation of electrons in the TiO_2 and of counterions in the electrolyte. In the case of bulk recombination, photocarriers recombine homogeneously throughout the titania film. For the case of bulk recombination, the electron quasi-Fermi level is flat. In the case of near-substrate recombination, electrons must diffuse to a near-substrate region. The corresponding gradient in E_{Fe} must be considered in interpreting V_{OC} .

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bination. In the present work, we studied several samples with good photovoltaic properties prepared at the NREL Lab; for all of these samples, we conclude that near-substrate recombination is a better explanation of the measurements than bulk recombination. The near-substrate recombination might involve the dense space charge in titania particles closest to the substrate,^{2,8,9} which would retain consistency with the results excluding direct substrate-electrolyte recombination.

The present conclusion disagrees with that drawn in nearly all previous studies,^{2,3,10} except those mainly done with very fast redox couples.¹⁰ Although general conclusions about recombination in dye-sensitized cells must await study of a broader range of cells, we believe that this disagreement in conclusions primarily reflects the very different arguments and methods involved. We suggest that, for the samples studied, the method used in the present work is definitive regarding the relative magnitudes of near-substrate and bulk recombination.

In this letter we report measurements from a cell with a 12.5 μm thick titania matrix made from 15–20 nm crystallites, and filled with (50 mM/0.8 M) iodine/dimethyl-hexyl-imidazodum iodide solution in methoxyacetonitrile. Several other samples of varying thickness were also studied with comparable results; additional properties of these particular samples have been given in a previous paper.⁶ They were illuminated from the substrate side by a laser diode (685 nm, <20 mW). This wavelength of light is only weakly absorbed by the dye molecules and creates nearly homogeneous photocarrier generation throughout the cell. The incident light intensity is sinusoidally modulated; we write the time-dependent part $\Delta\tilde{G}(t)$ of the total generation rate per unit of substrate area as $\Delta\tilde{G}(t) = \Delta G e^{2\pi i f t}$, where ΔG is the amplitude of the modulation, and f is the frequency.

Photocurrents reported here were measured under short-circuit conditions. The linear photocurrent response to $\Delta\tilde{G}(t)$ has the form $[\Delta\tilde{j}(f)]\exp(2\pi i f t)$, where the “complex amplitude” $\Delta\tilde{j}(f)$ allows for a phase shift between the photocurrent response and the generation rate. We refer to $\Delta\tilde{j}(f)$ as the intensity-modulated photocurrent (IMPS) signal.

The photomodulated, relative transmittance signal $\Delta T/T$ was measured at 950 nm (16 nm monochromator bandpass) with a Si p - i - n photodiode. The wavelength was chosen to lie beyond the absorption bands of the dye and of I_3^- ;^{7,11} an optical filter was used to eliminate the stray light from the 685 nm laser beam.

In Fig. 2 we present the IMPS measurements $\Delta\tilde{j}(f)$ as a function of modulation frequency, as well as the simultaneously measured IMIS measurements under short-circuit condition. We have normalized the IMPS signal $\Delta\tilde{j}(f)$ for finite frequency by the value $\Delta\tilde{j}_0$ at 0.4 Hz (the “low frequency limit”). The broad interpretation of the IMPS measurements is well established. The photocurrent may be interpreted as the rate of arrival of electrons at the electrodes due to ambipolar diffusion of electrons coupled to counterion charges.⁶ The decline in the signal amplitude higher modulation frequencies, as well as the phase shift (the shift of amplitude from the real to the imaginary component), occur when there is insufficient time in one modulation cycle for electrons to diffuse to the cell substrate. This effect has been

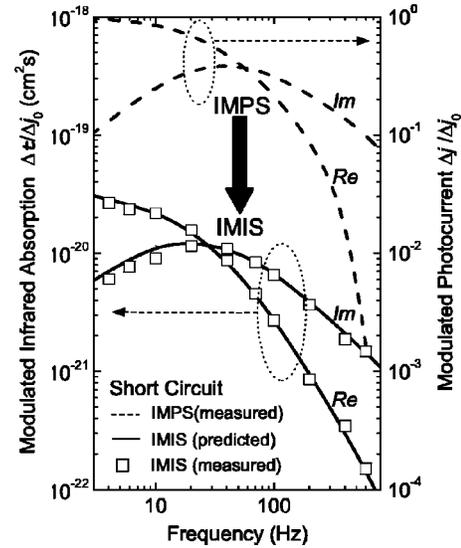


FIG. 2. Relationship of intensity-modulated photocurrent (IMPS) and intensity-modulated infrared (IMIS) transmittance measurements under short-circuit conditions. Dashed lines are the IMPS signals $\Delta\tilde{j}(f)$; real (Re) and imaginary (Im) parts are illustrated. The open squares indicate IMIS signals $\Delta\tilde{\tau}(f)$ under the same conditions. The solid lines are predictions from the IMPS spectra from the IMIS measurements using Eq. (3). The dc photocurrent was 2.7 mA/cm².

used by several authors to obtain a diffusion coefficient estimate,^{6,12,13} a typical diffusion coefficient (under illumination generating 1 mA/cm² photocurrent in a 10 μm cell) is 1×10^{-4} cm²/s.

We now turn to the intensity-modulated infrared transmittance IMIS. If we can assume that the local change in the optical properties of the film is proportional to the density of photoinjected electrons at this point, we can derive a simple equation relating IMPS and IMIS. We simplify by assuming that the relative transmittance change $\Delta T/T$ is proportional to the total, areal electron density N in the TiO₂ film:

$$\frac{\Delta T(\nu)}{T} = -\sigma(\nu)(N), \quad (1)$$

where e is the electronic charge and $\sigma(\nu)$ is an optical cross section (as a function of optical frequency ν). This equation is equivalent to the assumption of local proportionality when $\Delta T/T \ll 1$. The particle continuity equation connects the total electron density N and the current density $j(t)$ which exits the layer at the collecting electrode:

$$\frac{dN(t)}{dt} = G(t) - j(t), \quad (2)$$

where G is the photogeneration density (per unit area of substrate), and we have assumed that there is no recombination in the bulk of the TiO₂ matrix at short circuit.

Using the same approach as for $\Delta\tilde{j}(f)$, we shall write the measured relative transmittance as a complex amplitude $\Delta\tilde{\tau}(f)$, which we refer to as the “intensity-modulated infrared” (IMIS) signal. For a sinusoidally modulated photogeneration rate $\Delta\tilde{G}(t) = \Delta G e^{2\pi i f t}$, it can be shown with Fourier analysis that the expression relating the IMPS and IMIS signals $\Delta\tilde{j}(f)$ and $\Delta\tilde{\tau}(f)$ is:

$$\frac{\Delta\tilde{t}(f)}{\Delta\tilde{j}(0)} = \frac{\sigma}{2\pi if} \left[1 - \frac{\Delta\tilde{j}(f)}{\Delta\tilde{j}(0)} \right]. \quad (3)$$

Our IMIS measurements are presented as the symbols in Fig. 2; they appear to be consistent with previous IMIS work.⁷ In the figure we also show the prediction for IMIS based on the IMPS measurements and Eq. (3); the optical cross-section σ was chosen as a “best-fit” to be 0.6×10^{-17} cm². The predicted curve and the measurements agree with an error of about 10%. The magnitude for σ is in good agreement with earlier reports.^{7,14,15} Note that the present analysis accounts fairly well for the fact, noticed earlier by Franco *et al.*,⁷ that “typical” time constants for IMPS are substantially faster than those for IMIS.

It may be useful to reiterate the three assumptions which underlie this success in accounting for the IMIS signals under short-circuit conditions. First, we identified the currents with arrival of electrons at the substrate; essentially all the motion of photocarriers occurs under ambipolar diffusion conditions, and is thus not detected as a displacement current. Second, we assumed that the modulated infrared signal was proportional to the areal density of photoinjected electrons; we cannot distinguish between intraband optical transitions of electrons in TiO₂ and optical effects in the electrolyte. Finally, we assumed that recombination was negligible; all photocharge detected from infrared measurements ultimately arrived at the collecting electrode and was detected as a photocurrent.

We now turn to measurements under open-circuit conditions, which necessarily probe photocarrier recombination. Figure 3 shows IMIS measurement under the same illumination as for Fig. 2, but under open-circuit conditions. We also illustrate predictions from two different recombination models; we emphasize that neither model’s predictions were adjusted in any way to “fit” the open-circuit measurements. The model we denote “near-substrate recombination” simply reproduces the predictions for the IMIS signal from the short-circuit case. Under open-circuit conditions, this model implies that recombination is a “two-step” process: photocarriers first diffuse to the near-substrate region, and then recombine immediately. As evident, this model gives a good account for the open-circuit IMIS signal at high frequencies, but shows a deviation at low frequencies. We also present the predictions of the homogeneous recombination model.^{3,7} For this model, the modulated areal density of photoinjected electrons (ΔN) can be related to the separately measured photovoltage modulation $\Delta V(f)$ and capacitance C (per unit of substrate area):

$$\Delta\tilde{t}(f) = \sigma\Delta N(f) = \sigma[C\Delta V(f)/e]. \quad (4)$$

Since the optical cross-section σ was determined from the short-circuit measurements, there are no adjustable parameters in this prediction for $\Delta\tilde{t}(f)$; we used the capacitance C measured at 1 Hz. For this model, we find that the predicted time constant for IMIS ($1/2\pi f_{\max}$) is about 4 times longer than the measured value, and that the signal strength at higher frequencies is 30 times too small.

Based on these comparisons, we conclude that recombination occurs predominantly near the substrate for the sev-

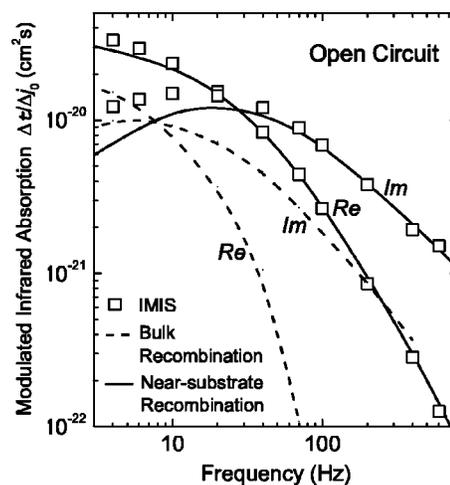


FIG. 3. Intensity-modulated infrared transmittance (IMIS) signals under open-circuit conditions. Symbols indicate measurements taken under the same illumination conditions as for Fig. 2. The lines show predictions for two recombination models (solid lines: very fast recombination occurring only in the near-substrate region; dashed lines: homogeneous recombination throughout the film). The open-circuit photovoltage V_{OC} was 0.65 V; the short-circuit current density was 2.7 mA/cm².

eral samples we have examined. Figure 3 does exhibit significant deviations between the measurements and the near-substrate recombination model at low frequencies. We attribute this effect to a noninfinite recombination rate in the near substrate region. Apparently, electron recombination at the titania/electrolyte interfaces in this region is a few times slower than the diffusion process which delivers electrons to it. This near-coincidence surprises us, and should certainly be a subject of further study, as should be the relative prevalence of bulk and near-substrate recombination in a wider range of samples.

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