

# Charge Transport and Back Reaction in Solid-State Dye-Sensitized Solar Cells: A Study Using Intensity-Modulated Photovoltage and Photocurrent Spectroscopy

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Solid-state dye-sensitized solar cells employing spiro-MeOTAD [2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenyl-amine)-9,9'-spirobifluorene] as a hole transport phase were studied by intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS) over a wide range of illumination intensity. The IMPS and IMVS responses provide information about charge transport and electron–hole recombination, respectively. For the range of light intensities investigated, the dynamic photocurrent response appears to be limited by the transport of electrons in the nanocrystalline TiO<sub>2</sub> film rather than by the transport of holes in the spiro-MeOTAD. The diffusion length of electrons in the TiO<sub>2</sub> was found to be  $4.4 \times 10^{-4}$  cm. This value was almost independent of light intensity as a consequence of the fact that the electron diffusion coefficient and the rate constant for electron–hole recombination both increase in the same way with light intensity (proportional to  $I_0^{0.64}$ ).

## Introduction

Dye-sensitized nanocrystalline solar cells are currently under intensive investigation for application as low cost photovoltaic devices. In this type of device, light is absorbed by dye molecules attached to the surface of a nanocrystalline wide band gap oxide, resulting in injection of electrons into the conduction band of the semiconductor. Photoinduced charge carrier generation has been shown to be very efficient for a cell consisting of a thin dye-sensitized TiO<sub>2</sub> film in contact with the organic hole conductor spiro-MeOTAD [2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenyl-amine)-9,9'-spirobifluorene].<sup>1</sup> The performance of early devices was limited by interfacial charge recombination.<sup>2</sup> This major loss mechanisms could be reduced by blending the spiro-MeOTAD matrix with a combination of tert.-butylpyridine (tBP) and Li[CF<sub>3</sub>SO<sub>2</sub>]<sub>2</sub>N, yielding devices with an significantly improved device performance.<sup>3</sup>

The present contribution describes a study of spiro-MeOTAD dye-sensitized solar cells by intensity-modulated photocurrent spectroscopy (IMPS)<sup>4–6</sup> and intensity-modulated photovoltage spectroscopy (IMVS).<sup>7,8</sup> IMPS measures the periodic photocurrent response of the cell to a small sinusoidal perturbation of the light intensity superimposed on a larger steady background level. The IMVS experiment uses the same intensity perturbation but measures the periodic modulation of the photovoltage (i.e., the difference in Fermi level in the dark  $E_F$  and the quasi Fermi level under illumination  $nE_F$ ). IMPS provides information about the dynamics of charge transport and back reaction under short circuit conditions, whereas the IMVS response is determined by the electron lifetime under open circuit conditions. These methods have been applied previously to study electrolyte-based dye-sensitized cells, where diffusive “hole transport” by triiodide ions is facile, whereas electron transport in the TiO<sub>2</sub> appears to be slow and trap-controlled.

One of the most striking features of the behavior of electrolyte-based dye-sensitized cells is the fact that their dynamic response becomes slower as the light intensity is reduced. This can be seen in the photocurrent and photovoltage responses to stepped illumination. The present study sets out to discover if solid-state cells exhibit a similar intensity dependence of the response time and whether electron (or hole) transport limits device performance. The results show that the electron diffusion coefficient and the rate constant for the back reaction of electrons with holes in the organic hole conductor both increase with light intensity in the same way. No evidence was obtained for limitation of the dynamic photocurrent response by hole transport. The electron diffusion length in the cells was found to be greater than 4  $\mu$ m. This value suggests that efficient cells can be constructed with TiO<sub>2</sub> layer thicknesses up to 4  $\mu$ m, provided that no other charge transport limiting problems interfere, such as incomplete pore filling for increased layer thicknesses.

## Experimental Section

The dye-sensitized cells were prepared on SnO<sub>2</sub>:F coated glass substrates (Asahi, 10  $\Omega$ /square). A spray pyrolysis technique<sup>9</sup> was used to coat the conducting glass with a thin compact layer of TiO<sub>2</sub> in order to prevent electron–hole recombination arising from direct contact between the hole conductor and the highly doped SnO<sub>2</sub> layer. A 2  $\mu$ m mesoporous TiO<sub>2</sub> layer was deposited by screen-printing onto this compact layer. The TiO<sub>2</sub> electrodes were dye-coated by soaking them for 8 h in a  $5 \times 10^{-4}$  M solution of (Bu<sub>4</sub>N)<sub>2</sub>[Ru(dcbpyH)<sub>2</sub>(NCS)<sub>2</sub>] in CH<sub>3</sub>CN:*t*-butanol (50:50 vol %) at room temperature. The hole conductor matrix was applied by spin-coating a solution of spiro-MeOTAD in chlorobenzene, containing Li[CF<sub>3</sub>SO<sub>2</sub>]<sub>2</sub>N and tBP. Finally, a gold contact was deposited on the organic semiconductor film by evaporation.

The experimental setup for IMPS and the IMVS measurements have been described previously.<sup>7</sup> Intensity-modulated measurements were carried out using a Solartron 1250 frequency

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response analyzer, which was used to drive a LED and to measure the optoelectronic transfer functions. The LED ( $\lambda = 480$  nm) provided both the dc and ac components of the illumination. The modulation depth of the ac component superimposed on the dc light was 8%. The light intensity was varied using calibrated neutral density filters (Schott) and measured with a calibrated silicon photodiode. A range of light intensities was used that correspond to about 1/20 of 1 Sun because additional effects need to be considered at higher light intensities because of limited charge transport in the hole conducting medium.

## Model

The experimental IMPS data have been analyzed making use of a model developed for the electrolyte-based dye-sensitized cells. This theory has been discussed in detail elsewhere,<sup>4,5,10</sup> and only a brief overview is given here. Small amplitude perturbation superimposed on steady illumination allows linearization of the periodic photocurrent response, and the effects of trapping can be taken into account explicitly or by using the effective diffusion coefficient approximation. Electron transport in dye-sensitized TiO<sub>2</sub> solar cell can be described by a continuity equation

$$\frac{\partial n(x,t)}{\partial t} = G(x) + \frac{\partial J_n(x,t)}{\partial x} - R(x,t) \quad (1)$$

where  $n(x,t)$  is the local electron concentration. The first term on the right is the rate at which electrons are generated by photosensitization. The second term involving the electron current density  $J_n$  describes the electron transport in the mesoporous network. The last term takes into account the loss mechanism, i.e., recombination processes. Several models have been proposed to solve this equation,<sup>11–16</sup> which differ mainly in the treatment of the electron trapping processes in the TiO<sub>2</sub> network. In the present work, the model of Dloczik et al.<sup>4</sup> has been used which treats the effect of trapping by using an effective diffusion coefficient  $D_{\text{eff}} = D \cdot n_{\text{free}}/n_{\text{total}}$  to describe electron transport. In the limit of small amplitude modulation, the recombination term can be expressed as a first-order decay of the electrons characterized by a pseudo-first-order electron lifetime  $\tau_n$ . Because of the small TiO<sub>2</sub> particle size, which does not allow any band bending, electron transport in the TiO<sub>2</sub> is dominated by diffusion. Based on these assumptions, the continuity equation becomes

$$\frac{\partial n(x,t)}{\partial t} = \eta \alpha \exp(-\alpha x) + D_{\text{eff}} \frac{\partial^2 n(x,t)}{\partial x^2} - \frac{n(x,t) - n_0}{\tau_n} \quad (2)$$

where  $\alpha$  is the absorption coefficient determined by the dye coverage and the surface area/volume ratio of the nanocrystalline electrode,  $\eta$  is the electron injection efficiency, and  $n_0$  is the electron concentration in the dark. Equation 2 has been solved assuming that electrons are extracted at the back contact over a potential-dependent energy barrier with a characteristic extraction rate (see Supporting Information). For high values of the extraction rate constant, the current becomes diffusion controlled. The predicted IMPS response appears in the lower complex plane as a consequence of the phase lag arising from the time required for electrons to diffuse to the contact. The measured external current can be obtained by multiplication of the theoretical internal current by an attenuation factor

$$T = \frac{1 - i\omega RC}{1 + \omega^2 R^2 C^2} \quad (3)$$

Here,  $R$  is the series resistance of the contacts and  $C$  is the capacitance of the substrate electrode.

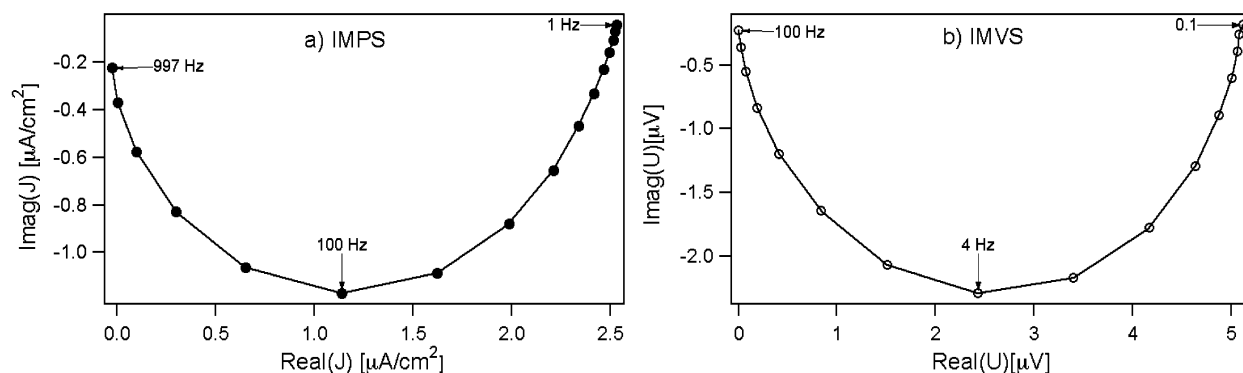
Code plots, as well as the complex plane plots were fitted using a nonlinear-least-squares fit program (“Igor” software, Wavemetrics), based on the Levenberg–Marquardt algorithm. The constant parameters in the fits of the current responses were derived independently. An initial estimate for the absorption coefficient  $\alpha = A/d$  was determined from absorption spectroscopy and film thickness measurements (Alpha step). Light scattering of the two  $\mu\text{m}$  thick TiO<sub>2</sub> films is negligible. Reflection at the 20 nm thick gold film was neglected. Light absorption by the hole conductor radical cation was considered empirically by defining an effective absorption coefficient, which was derived from the fit of the highest light intensity IMPS response. A high value of the extraction constant ( $10^4 \text{ cm s}^{-1}$ ) was chosen to correspond to diffusion-controlled electron extraction under short circuit conditions.  $D_{\text{eff}}$  and  $\tau_n$  were varied to obtain the best fit to the measured curve. The values for  $R$  and  $C$  were obtained by impedance measurements under comparable illumination conditions. Consideration of the attenuation factor improved the fit of the curve at high frequencies but changed the value for the diffusion coefficient only slightly.

The theory of the IMVS response has been discussed in detail by Schlichthörl.<sup>8</sup> For the present analysis, it is sufficient to note that the small amplitude photovoltage response is characterized by a first-order electron lifetime  $\tau_n$ , which is the inverse of the pseudo-first-order rate constant for electron hole recombination. The IMVS response is therefore a semicircle in the lower complex plane with a minimum at  $\omega = \tau_n^{-1}$ .

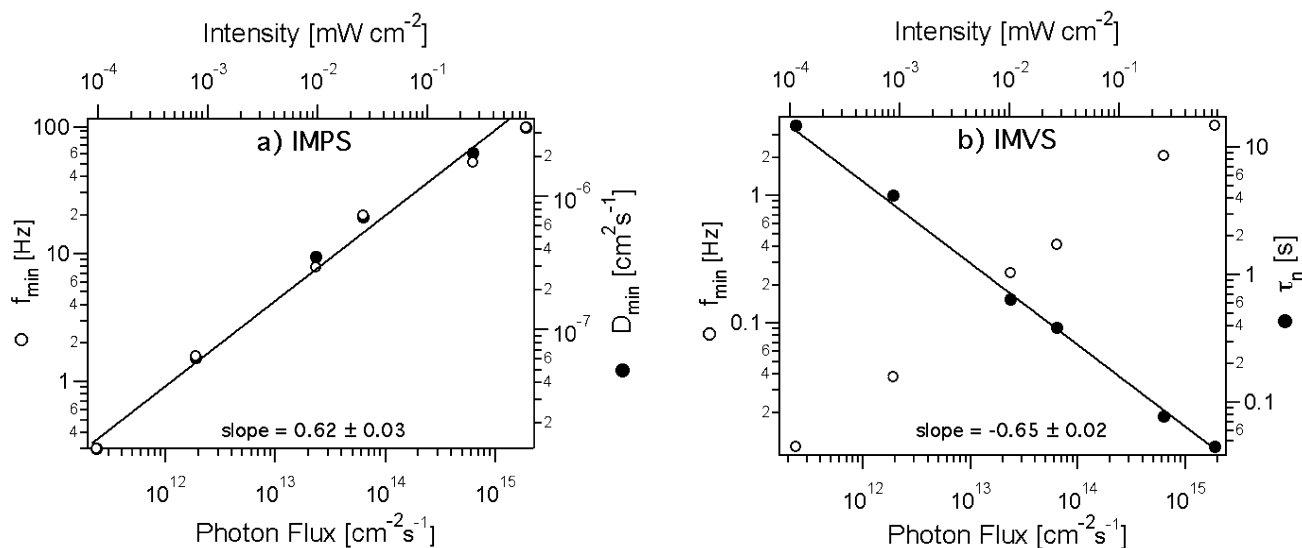
## Results and Discussion

IMVS and IMPS measurements were carried out over a range of illumination intensities of 4 orders of magnitude. Figure 1 illustrates typical complex plane plots for the IMVS and IMPS responses at the highest light intensity used. Both photocurrent and photovoltage lag behind the illumination, leading to a response in the fourth quadrant (positive real, negative imaginary) of the complex plane. In the absence of electron–hole recombination, the phase shift of the IMPS semicircle is a result of the time delay between the generation and collection of charge carriers. At low frequencies, the IMPS plots converge to a point on the real axis that corresponds to the steady-state photocurrent. At high frequencies the modulated photocurrent tends to zero, indicating that the modulation frequency is faster than the relaxation of the charge carrier density by transport to the contacts and back reaction. In the case of the IMVS experiment, the response is semicircular and the phase lag is due to relaxation of electrons by back reaction with cations in the hole conductor matrix, which one may assume are in excess.

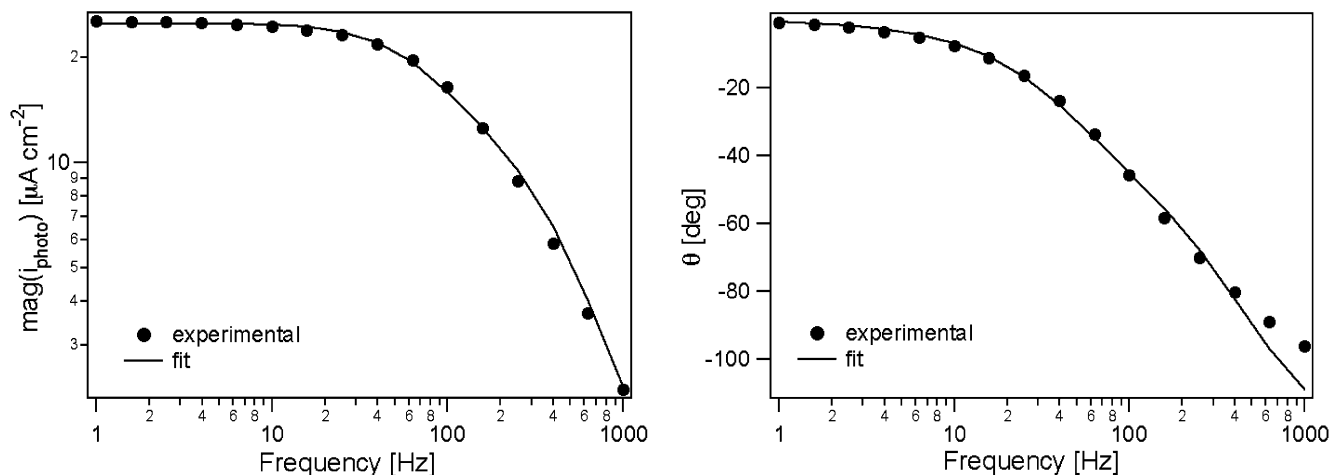
It was found that changing the intensity of the incident illumination did not influence the shape of the IMPS and the IMVS plots. However, the frequency of the minima in both types of plots was observed to decrease with reduced light intensity. This variation of the minimum frequencies as function of the incident photon flux is illustrated in Figure 2 in double logarithmic representation. For both experiments, a linear correlation is observed with a slope of 0.63 for IMPS and 0.65 for IMVS. The electron lifetime can be obtained from the IMVS plot by setting  $\tau_n = (2\pi f_{\text{min}}(\text{IMVS}))^{-1}$ . Therefore, the dependence of  $\tau_n$  on the light intensity has the same slope as the  $\log(f_{\text{min}}(\text{IMVS})) = f(\log(I_0))$  but with inverse sign. An order of



**Figure 1.** Typical IMPS (a) and IMVS (b) responses for the solid-state solar cell ( $I_0 = 1.9 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ ). The hole conductor film was deposited using a spin-coating solution containing 0.1 M spiro-MeOTAD in chlorobenzene, 14 mM  $\text{Li}[\text{CF}_3\text{SO}_2]_2\text{N}$ , 0.12 M tBP, and 0.4 mM  $\text{N}(p\text{-C}_6\text{H}_4\text{-Br})_3\text{SbCl}_6$ .



**Figure 2.** Light intensity dependence of  $f_{\min}(\text{IMPS})$  (a) and  $f_{\min}(\text{IMVS})$  (b). On the right axis the calculated parameters are given, i.e., the diffusion coefficient for the IMPS experiment and the lifetime for the IMVS experiment.



**Figure 3.** Short circuit IMPS response represented in the form of Bode plots (●). The IMPS fit (fit parameters:  $D_n = 3.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ,  $\tau_n = 4.5 \text{ ms}$ ,  $k_{\text{ex}} = 10^5$ ,  $\alpha = 2200 \text{ cm}^{-1}$ ,  $R = 23 \Omega$ ,  $C = 1.6 \times 10^{-5} \text{ F}$ ) is shown as a line.

magnitude estimate of a mean transit time for photogenerated electrons can be obtained from the frequency minimum in the complex plane IMPS plot:  $\tau_d = (2\pi f_{\min}(\text{IMPS}))^{-1}$ .  $\tau_n$  and  $\tau_d$  differ at least 1 order of magnitude, reflecting the difference between mixed diffusion/recombination control under short circuit conditions to pure recombination control under open circuit potential. At short circuit and for homogeneously absorbed light, the electron diffusion coefficient can be estimated

from the relation  $D_n = d^2/4\tau_d$  where  $d$  is the layer thickness of the nanocrystalline  $\text{TiO}_2$ . A more satisfactory approach to determine the diffusion coefficient is to fit of the IMPS data based on the model discussed above. Figure 3 compares examples of theoretical and experimental IMPS plots for a photon flux of  $I_0 = 1.9 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ . The diffusion coefficients obtained from the fitted IMPS responses at different light intensities are summarized in Figure 2a. The trends in the

diffusion coefficient and the electron lifetime with light intensity (Figure 2b) are similar to those reported for the electrolyte cell: electron diffusion becomes faster with increasing light intensity, whereas the electron lifetime decreases. The fact that the values obtained for the electron diffusion coefficient in the solid-state solar cell are similar to those determined for electrolyte cells, confirms that internal electric fields are negligible for the light intensity range studied.

The values of electron diffusion coefficient and electron lifetime can be used to calculate the electron diffusion length,  $L_n = (D_n \tau_n)^{1/2}$ , which is determined by the competition between electron transport and back reaction.<sup>6,7</sup> A value of  $L_n = 4.4 \mu\text{m}$  was obtained, which does not alter more than  $\pm 0.5 \mu\text{m}$  over the whole range of measured intensities. The diffusion length does not change with light intensity which arises from the fact that the electron lifetime and diffusion coefficient have nearly the same dependence on light intensity but with opposite sign. This suggests strongly that the rate-limiting step in electron transport and in the back reaction is the same, namely trap limited hopping. In the case of electrolyte cells, by contrast, the power laws describing the intensity dependences of the electron diffusion coefficient and lifetime do not compensate each other exactly, so that the IPCE is weakly intensity dependent. In this case, it seems likely that the back reaction of electrons with tri-iodide ions takes place under mixed kinetic/transport control. The electron diffusion length for electrolyte cells in the same light intensity range as that used in the present work has been reported to vary between 10 and 20  $\mu\text{m}$ .<sup>7</sup> The smaller electron diffusion length in the present cells reflects the shorter electron lifetime in the solid-state cell compared with the electrolyte cell.

In the case of electrolyte cells, the variation of the diffusion coefficient with incident photon flux has been attributed to trap limited electron transport in the porous  $\text{TiO}_2$ .<sup>4,16,17</sup> In the dark under open circuit conditions, the Fermi level (and hence trap occupancy) in the  $\text{TiO}_2$  particles is determined by electron exchange with redox mediator. Under illumination, the trap occupancy changes with the position of the quasi Fermi level for electrons. As the quasi Fermi level moves toward the conduction band with increasing light intensity, deep traps will be filled so that they no longer retard electron transport. Exchange with shallow traps is much faster, so that the effective diffusion rate becomes higher. The results obtained for the solid-state cell indicate that the mechanism of electron transport in the  $\text{TiO}_2$  is the same as in the electrolyte cells for the range of light intensities investigated.

The electron lifetime for the  $\text{I}^-/\text{I}_3^-$  electrolyte cell has been found to vary with the inverse square root of the light intensity. This behavior has been rationalized in terms of a two-step recombination reaction between electrons and tri-iodide, which is second order in electron concentration.<sup>18</sup> By contrast, spiro-MeOTAD is expected to behave as a one-electron redox system, so that the rate constant for the back reaction of electrons with holes should be first order and independent of light intensity. In fact, as discussed above, the results show a clear dependence of the recombination rate constant on the light intensity. Similar behavior has been observed for other one-electron redox systems, such as  $\text{CuI}$  and polyaniline.<sup>19</sup> This indicates that electron trapping may exert a significant effect on the rate constant for electron transfer. Nelson et al.<sup>20</sup> have suggested that trapping alone could lead to the recombination behavior at low intensities observed in electrolyte cells. In the case of the solid-state cells, the back reaction certainly appears to be controlled by the rate of electron transport in the  $\text{TiO}_2$  film rather than the transport properties of the dye mediator system.

## Conclusions

Values of the electron diffusion coefficient and electron lifetime in the spiro-MeOTAD [2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenyl-amine)-9,9'-spirobifluorene] solid-state dye-sensitized solar cell have been derived from IMPS and IMVS measurements. The light intensity dependence of these parameters indicates that the transient response of the cell for less than 1  $\text{mW cm}^{-2}$  appears to be dominated by electron transport in the  $\text{TiO}_2$  rather than hole transport in the organic material. The rate constant for electron hole recombination is also intensity dependent, and the data presented here provide compelling evidence that recombination is controlled by electron transport in the  $\text{TiO}_2$ . An intensity independent electron diffusion length of 4.4  $\mu\text{m}$  has been determined, which is by a factor of 4 lower than in the electrolyte cell but two times higher than the  $\text{TiO}_2$  layer thickness. This indicates that electron collection in the cell is very efficient at low light intensities.

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**Supporting Information Available:** Details of the mathematical solution of eq 2 (1 page). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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