Optical description of solid-state dye-sensitized solar cells. II. Device optical modeling with implications for improving efficiency

Journal of Applied Physics, 2009; 106(7):073112-1-073112-6

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16 June 2021

http://hdl.handle.net/2440/64529
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Cite as: J. Appl. Phys. 106, 073112 (2009); https://doi.org/10.1063/1.3204985
Submitted: 12 May 2009 . Accepted: 10 July 2009 . Published Online: 14 October 2009

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Optical description of solid-state dye-sensitized solar cells. II. Device optical modeling with implications for improving efficiency

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(Received 12 May 2009; accepted 10 July 2009; published online 14 October 2009)

We use the optical transfer-matrix method to quantify the spatial distribution of light in solid-state dye-sensitized solar cells (DSCs), employing material optical properties measured experimentally in the accompanying article (Part I) as input into the optical model. By comparing the optical modeling results with experimental photovoltaic action spectra for solid-state DSCs containing either a ruthenium-based dye or an organic indoline-based dye, we show that the internal quantum efficiency (IQE) of the devices for both dyes is around 60% for almost all wavelengths, substantially lower than the almost 100% IQE measured for liquid DSCs, indicating substantial electrical losses in solid-state DSCs that can account for much of the current factor-of-two difference between the efficiencies of liquid and solid-state DSCs. The model calculations also demonstrate significant optical losses due to absorption by 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9'-'spirobifluorene (spiro-OMeTAD) and TiO2 in the blue and to a lesser extent throughout the visible. As a consequence, the more absorptive organic dye, D149, should outperform the standard ruthenium complex sensitizer, Z907, for all device thicknesses, underlining the potential benefits of high extinction coefficient dyes optimized for solid-state DSC operation. © 2009 American Institute of Physics. [doi:10.1063/1.3204985]

I. INTRODUCTION

Dye-sensitized solar cells (DSCs) (Ref. 1) provide a cheap and efficient2 alternative to traditional crystalline silicon solar cells. Standard DSCs use a mesoporous TiO2 semiconductor matrix covered with a monolayer of a light-absorbing dye and filled with a redox active electrolyte. Despite the relatively high efficiencies of liquid electrolyte DSCs of more than 11%,2 concerns over the stability of the electrolyte. Incomplete filling of the mesoporous TiO2 matrix with a redox couple, which is responsible for a large fraction of the losses, has been observed.5 By comparing the model results with experimental photovoltaic action spectra for solid-state DSCs containing either a ruthenium-based dye or an organic indoline-based dye, we show that the internal quantum efficiency (IQE) of the devices for both dyes is around 60% for almost all wavelengths, substantially lower than the almost 100% IQE measured for liquid DSCs, indicating substantial electrical losses in solid-state DSCs that can account for much of the current factor-of-two difference between the efficiencies of liquid and solid-state DSCs. The model calculations also demonstrate significant optical losses due to absorption by 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9'-'spirobifluorene (spiro-OMeTAD) and TiO2 in the blue and to a lesser extent throughout the visible. As a consequence, the more absorptive organic dye, D149, should outperform the standard ruthenium complex sensitizer, Z907, for all device thicknesses, underlining the potential benefits of high extinction coefficient dyes optimized for solid-state DSC operation.

In this article, we quantify the spatial distribution of light in DSCs by using the optical transfer-matrix method.5 Crucially, we employ, as input into our model, optical properties (namely, the complex refractive indices) of the various layers that make up a DSC that were accurately measured in the accompanying article (Part I).9 The article is organized as follows: in Sec. II A, the essential features of the optical transfer-matrix model are presented; in Sec. II B, the experimental procedures by which SDSCs were fabricated and measured are presented; finally, in Sec. III, the optical model is used to calculate the absorption-limited maximum external quantum efficiency, maximum short-circuit current, and spatial light distribution in SDSCs containing either a ruthenium-based dye (termed Z907)10 or an organic indoline-based dye (termed D149).8,11 By comparing the model results with the experimental measurements, electrical and optical losses in SDSCs are quantified.

II. METHODS

A. Model

SDSCs consist of multiple thin film layers with different optical properties. In the optical transfer-matrix model8 used in this work to calculate the distribution of light intensity in...
SDSCs, the layers are assumed for simplicity to be parallel, smooth, and of uniform thickness. The transfer-matrix method accounts for reflection and transmission at interfaces, absorption within the layers, and optical interference between ingoing and outgoing optical electric fields, which can be significant for the small layer thicknesses (<2 μm) in SDSCs. The transfer-matrix method as applied to solar cells has been described in detail elsewhere,12–16 and so only the essential features of the model will be described here. Figure 1 illustrates schematically the optical model of the solar cell. The only parameters required by the model are the complex index of refraction $n_\text{eff}$ of the active layer, which includes absorption by the TiO$_2$ matrix, the organic hole conductor spiro-OMeTAD, and the dye. A zeroth-order approximation (which is almost certainly an overestimate) for the light-absorption-limited maximum external quantum efficiency ($\text{EQE}_{\text{max}}$) is that all light absorbed in the active layer is converted into photocurrent, i.e., $\text{EQE}_{\text{max}} = D_{\text{AL}} \times 100\%$, where $D_{\text{AL}}$ is the total dissipation (relative to $I_0$) in the active layer. To arrive at a more accurate approximation of this upper bound on EQE, we assume that only absorption by the dye can be converted into photocurrent. The complex indices of refraction, $n_{\text{AL}}$ and $n_{\text{AL-dye}}$, respectively, for the active layer with dye (TiO$_2$ matrix + dye + spiro-OMeTAD) and without dye (TiO$_2$ matrix + spiro-OMeTAD) have been measured in the accompanying article (Part I). From Eqs. (1) and (2) $D_j \approx n_j k_j$, and so the proportion of the incident power dissipated in the dye, which is the $\text{EQE}_{\text{max}}$ in this approximation, can be estimated as

$$\text{EQE}_{\text{max}} = \frac{(n_{\text{AL}} k_{\text{AL}} - n_{\text{AL-dye}} k_{\text{AL-dye}})}{n_{\text{AL}} k_{\text{AL}}} \times \text{EQE}^0_{\text{max}},$$

(3)

The internal quantum efficiency (IQE) can be estimated as $\text{IQE} = \text{EQE} / \text{EQE}_{\text{max}}$, where EQE is the experimental external quantum efficiency. IQE is the efficiency by which photons absorbed by the dye are converted into photocurrent and can therefore be regarded as the electrical efficiency of the device. The maximum possible short-circuit current under one sun was calculated with

$$J_{\text{sc,max}} = e \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} \text{EQE}_{\text{max}}(\lambda) b(\lambda) d\lambda,$$

(4)

where $e$ is the elementary charge and $b(\lambda)$ is the Am.1.5 solar photon flux (total irradiance of 1000 W/m$^2$). The internal quantum efficiency and maximum short-circuit current, IQE$^0$ and $J_{\text{sc,max}}^0$, respectively, corresponding to EQE$_{\text{max}}$ were calculated by analogous methods.

It should be noted in passing that the effect of scattering is neglected in this optical model, but it is not expected to be significant in the SDSCs studied because highly transparent titania pastes were used. The effect of scattering should be small based on an estimate of the scattering rate scaling as $a^3 / \lambda^4$,18 where $a$ is the size of the scattering particles (10–20 nm in the homogeneous titania paste used in the SDSCs studied), which is an order of magnitude smaller than the wavelength $\lambda$. Confirming this prediction, the absorption spectra for the active layer filled with or lacking spiro-OMeTAD were found to be essentially identical outside the region in which the spiro-OMeTAD absorbs significantly (<420 nm),9 whereas the amount of scattering should differ substantially with and without spiro-OMeTAD, due to the reduction in refractive index contrast between the pores and the TiO$_2$ particles on addition of the organic hole conductor.

The SDSCs studied with this optical model comprised five layers, in addition to the soda-lime glass substrate: (1) fluorine-doped tin oxide (FTO); (2) compact TiO$_2$; (3) active layer (TiO$_2$+spiro-OMeTAD+dye); (4) spiro-OMeTAD capping layer; and (5) Ag electrode. The complex indices of refraction of the compact TiO$_2$, mesoporous TiO$_2$ (dyed and bare), spiro-OMeTAD, and Ag layers were measured experimentally in the accompanying article (Part I). The complex refractive index of specular FTO thin films
measured by Rovira and Collins was used for FTO (with values >800 nm obtained by linear extrapolation) and that for BK7 glass at 25 °C (Ref. 20) was used for the glass substrate. SDSCs with two different dyes, the organic indoline-based dye D149 (Refs. 6, 11, and 21) and the ruthenium-based dye Z907 (Ref. 10) were studied. Layer thicknesses were chosen to match those of the experimentally measured devices: 400 nm for FTO, 100 nm for compact TiO2, 1.4 μm (Z907) or 2 μm (D149) for the active layer, 200 nm for spiro-OMeTAD, and 200 nm for the Ag electrode.

B. Experimental

FTO-coated glass sheets (15 Ω/□, Nipon SG) were etched with zinc powder and HCl (4V) to give the required electrode pattern. The sheets were subsequently cleaned with soap (2% Helmanex in water), distilled water, acetone, ethanol, and finally treated under an oxygen plasma for 10 min to remove any organic residues. The FTO sheets were then coated with a compact layer of TiO2 (100 nm) by aerosol spray pyrolysis deposition at 450 °C using oxygen as the carrier gas. A homemade TiO2 nanoparticle paste was doctor bladed onto the compact TiO2 to give dry film thicknesses between 1.4 and 2 μm, governed by the height of the doctor blade. These sheets were then slowly heated to 500 °C (ramped over 30 min) and baked at this temperature for 30 min under an oxygen flow. After cooling, the sheets were cut into slides of the required size and stored in the dark until further use. The final sintered film porosity was 0.6 as determined by nitrogen absorption. Prior to fabrication of each set of devices, the nanoporous films were soaked in a 0.02 M aqueous solution of TiCl4 for 6 h at room temperature in the dark. After rinsing with de-ionized water and drying in air, the films were baked once more at 500 °C for 45 min under oxygen flow with subsequent cooling to 70 °C and placed in a dye solution overnight. The ruthenium-based dye used for sensitization was “Z907,” a thiacenine bipyridyl complex with hydrophobic side chains. The organic dye used for sensitization was “D149,” an indoline-based push-pull sensitizer with an exceptionally high extinction coefficient of ∼68 000 cm−1 M−1. The dye solutions comprised 0.5 mM of Z907 or 0.2 mM of D149 in acetonitrile and tert-butyl alcohol (volume ratio 1:1). The hole-transporting material used was spiro-OMeTAD, which was dissolved in chlorobenzene at a typical concentration of 180 mg ml−1. After fully dissolving the spiro-OMeTAD at 100 °C for 30 min, the solution was cooled and tert-butyl pyridine (tbp) was added directly to the solution with a volume-to-mass ratio of 1:26 μg mg−1 of LiTFSI ionic dopant was predissolved in acetonitrile at 170 mg ml−1, then added to the hole-transporter solution at 1:12 μg mg−1 of LiTFSI solution·spiro-OMeTAD. We note that no chemical oxidant was used in the hole-transporter.

The dye-coated mesoporous films were briefly rinsed in acetonitrile and dried in air for 1 min. A small quantity (20–70 μl) of the spiro-OMeTAD solution was dispensed onto each dye-coated substrate and left for 40 s before spin-coating at 2000 rpm for 25 s in air. The films were then placed in a thermal evaporator, where 150-nm-thick silver electrodes were deposited through a shadow mask under high vacuum (10−6 mbar). The device area was defined as the overlap between the anode and cathode and was approximately 0.05–0.16 cm2.

The photovoltaic action spectra were taken using light generated from a halogen lamp monochromatized and focused onto the solar cell at an approximate intensity of 100 W/m2. The photovoltage was generated from a halogen lamp monochromated and focused onto the solar cell at an approximate intensity of 100 W/m2. The photovoltage was generated from a halogen lamp monochromated and focused onto the solar cell at an approximate intensity of 100 W/m2. The photovoltage was generated from a halogen lamp monochromated and focused onto the solar cell at an approximate intensity of 100 W/m2.

FIG. 2. EQEmax from the optical model (dashed lines), EQE from experiment (circles+solid lines), and calculated IQE (squares+dotted lines) vs wavelength from the optical model for SDSCs containing the (a) Z907 dye (active layer thickness dAL=1.4 μm) and (b) D149 dye (dAL=2.0 μm). (c) and (d) are the same as (a) and (b), respectively, except that EQEmax and IQE have been replaced by the EQEmax and IQEmax, which were calculated assuming all light absorbed in the active layer is converted into photocurrent. The error bars in IQE and IQEmax were calculated by assuming errors of ±0.0015 in k(λ) for the active layer.

III. RESULTS AND DISCUSSION

A. Maximum external quantum efficiency

The calculated EQEmax, experimentally measured EQE, and calculated IQE for SDSCs containing the Z907 and the D149 dyes are shown in Figs. 2(a) and 2(b), respectively. The maximum external quantum efficiency (EQEmax) and internal quantum efficiency (IQEmax) calculated assuming that all light absorbed in the active layer is converted into photocurrent are shown in Figs. 2(c) and 2(d), respectively, for the Z907 and D149 dyes. Figures 2(a) and 2(b) show that despite the significant differences between EQE for the two dyes, IQE is approximately 60% in both cases for almost all wavelengths where EQE is measurable. The relative constancy of IQE with wavelength is to be expected, since IQE represents the electrical efficiency and should therefore be independent of optical parameters like the wavelength. Most importantly, this result suggests that the efficiency of SDSCs could be almost doubled if IQE were close to 100%, as it is in standard liquid DSCs. The positions of the oscillations in the experimental curve for EQE for the Z907 dye are reproduced well by the calculated EQEmax. The amplitude of the oscillations in the model curves are more pronounced than those in
the experimental curves because the model assumes perfectly flat interfaces between the layers, which is experimentally not the case.

If the total amount of light absorbed by the active layer is used to calculate EQE<sub>max</sub>, the obtained IQE<sup>0</sup> shows more variation with wavelength and essentially follows the EQE curve, as shown in Figs. 2(c) and 2(d). This occurs because IQE<sup>0</sup> does not account for optical losses within the spiro-OMeTAD and TiO<sub>2</sub> layers. Comparing EQE<sub>max</sub> with IQE<sub>0</sub> or IQE with IQE<sup>0</sup> in Figs. 2(a) and 2(c) or Figs. 2(b) and 2(d), it can be seen that a significant proportion of the absorbed light is lost to spiro-OMeTAD or TiO<sub>2</sub>, particularly at long wavelengths and for the less absorptive Z907 dye. This is strong evidence that the light absorbed in the spiro-OMeTAD or TiO<sub>2</sub> at long wavelengths does not contribute effectively to current generation. At short wavelengths (<450 nm), IQE for both dyes increases to almost 100%, whereas IQE<sup>0</sup> does not show a similar increase. To remind the reader, IQE only accounts for light absorbed in the dye and IQE<sup>0</sup> accounts for light absorbed in the whole active layer. This result suggests that the light absorbed by spiro-OMeTAD at these wavelengths, i.e., ground state absorption, is being transferred to the dye, for example, by Förster resonant energy transfer, causing an apparent increased efficiency. However, the relatively low IQE<sup>0</sup> at these wavelengths shows that a substantial proportion of the absorbed light (~40%) is not being converted into photocurrent.

At wavelengths longer than 680 nm for the Z907 dye and 640 nm for the D149 dye, the IQE is significantly reduced compared with the relatively constant value it has over most of the visible spectrum. In our calculation of IQE [from EQE<sub>max</sub> using Eq. (3)] we attempt to determine absorption in the dye rather than in the entire active layer. At the longer wavelengths, where the dye absorbance is reduced, the relative difference among the extinction coefficient of the dye, the spiro-OMeTAD/TiO<sub>2</sub> background, and the absolute error in the measurement combine to greatly increase the error in the calculation. Nevertheless, the value of IQE = 60% that is calculated throughout most of the visible spectrum falls outside of the error bars in the low absorbing region. One possible reason for this effect is that the optical properties of spiro-OMeTAD change with aging. Preliminary measurements that we have made suggest noticeable changes over time in the absorbance of spiro-OMeTAD at long wavelengths due to oxidation. Because the experimental photovoltaic action spectra and complex refractive indices in the optical model were measured at different times after layer deposition (soon after versus weeks later), the modeled optical characteristics at long wavelengths could differ from those of the fabricated devices. Another explanation for the reduced IQE between 650 and 800 nm is that the excited dye perhaps does not effectively transfer electrons to the TiO<sub>2</sub> near the absorption edge. There have been observations of “hot” electron transfer in dye-sensitized systems<sup>27,28</sup> and this could lead to a reduction in injection efficiency near the band edge if the excited state of the dye is close to or higher in energy than the TiO<sub>2</sub> conduction band. Without in-depth spectroscopic investigation, however, we can speculate no further on these points and, due to the significant measurement error in this low absorbing region, do not wish to draw solid conclusions here. We are, however, investigating this further.

### B. Maximum short-circuit current density

The maximum short-circuit current density J<sub>sc,max</sub> calculated by using Eq. (4), which assumes that only light absorbed in the dye contributes to photocurrent, is plotted in Fig. 3 as a function of the active layer thickness. Also shown in Fig. 3 is the maximum short-circuit current density J<sub>sc,max</sub> calculated assuming that all light absorbed in the active layer is converted into photocurrent. If all light absorbed by the dye, TiO<sub>2</sub>, and spiro-OMeTAD in the active layer is assumed to be converted into photocurrent, the maximum short-circuit current density J<sub>sc,max</sub> for both dyes approach the same value for large active layer thicknesses because essentially all of the light that is not reflected from the front of the device is absorbed by the active layer. However, if only light absorbed by the dye is assumed to contribute to photocurrent, the current density (J<sub>sc,max</sub>) is significantly lower, demonstrating that substantial losses occur in the SDSCs due to competitive absorption by spiro-OMeTAD and TiO<sub>2</sub>. The losses are more severe at all device thicknesses up to 20 µm for the less absorbing sensitizer, Z907, with the differences between the organic D149 dye and the Z907 ruthenium complex being most significant for thinner devices. Currently, the film thickness of a practical device is limited to around 2 µm due to problems with pore filling.<sup>29</sup> For thin films it is apparent that a higher extinction coefficient dye should be advantageous. Furthermore, our findings imply that regardless of film thickness, higher extinction coefficient dyes should be beneficial, since the light harvesting in the sensitizer competes with absorption in the rest of the medium. We note though that the observed differences here probably overestimate the true losses since our results do not take into...
account possible charge generation or energy transfer from the TiO$_2$ or spiro-OMeTAD. It should also be noted that the range of active layer thicknesses studied here far exceeds those achievable for SDSCs due to inadequate pore filling by the organic hole conductor for devices thicker than 2 $\mu$m.\textsuperscript{49,29}

Experimental data for the short-circuit current density as a function of active layer thickness for comparison with the calculated results in Fig. 3 do not currently exist for SDSCs containing the D149 or Z907 dye. But such data are available for SDSCs containing K68, a sensitizer that is spectroscopically almost identical to Z907. Figure 3 shows the experimentally measured EQE spectrum integrated over the AM1.5 solar spectrum for solid-state DSCs of varying thickness incorporating K68.\textsuperscript{29} The experimental points for K68 are all approximately 63\%–77\% of the calculated $J_{\text{sc,max}}$ for Z907 at the same thicknesses, comparable with the value of IQE $\approx$ 60\% that would be expected if IQE were constant across the spectrum, as our optical modeling results indicate to be approximately true. The agreement is not perfect, partly because IQE is not completely constant over the spectrum, in-creasing sharply for wavelengths around those for typical SDSCs

C. Spatial light distribution

The behaviors of the calculated maximum short-circuit current density in Fig. 3 and external quantum efficiency in Fig. 2 are more clearly understood by examining the calculated distribution of light intensity inside a SDSC. Figure 4 shows the squared magnitude of the optical electrical field, $|E(x)|^2$, as a function of the distance $x$ from the substrate/multilayer interface (in units of the squared magnitude of the electric field incident on the glass substrate, $|E_0|^2=380$ nm) in a DSC (a) containing no dye for a wavelength of $\lambda$ =380 nm and containing the D149 dye for (b) $\lambda$=530 nm and (c) $\lambda$ =640 nm. The dashed vertical lines demarcate the boundaries between (from left to right) the FTO (400 nm), TiO$_2$ compact (100 nm), active (2 $\mu$m), spiro-OMeTAD (200 nm), and Ag electrode (200 nm) layers. The active layer is also shaded in gray.

![Image](Image 352x522 to 520x742)

**FIG. 4.** Square of magnitude of calculated optical electrical field, $|E(x)|^2$, as a function of the distance $x$ from the substrate/multilayer interface (in units of the squared magnitude of the electric field incident on the glass substrate, $|E_0|^2=380$ nm) in a SDSC (a) containing no dye for a wavelength of $\lambda$ =380 nm and containing the D149 dye for (b) $\lambda$=530 nm and (c) $\lambda$ =640 nm. The dashed vertical lines demarcate the boundaries between (from left to right) the FTO (400 nm), TiO$_2$ compact (100 nm), active (2 $\mu$m), spiro-OMeTAD (200 nm), and Ag electrode (200 nm) layers. The active layer is also shaded in gray.

containing [Fig. 4(a)] no dye and containing the D149 dye for [Fig. 4(b)] 530-nm and [Fig. 4(c)] 640-nm light. Similar behavior to Figs. 4(b) and 4(c) is observed for the Z907 dye, although with less attenuation of the light intensity near the absorption maximum, due to the lower absorption coefficient of the Z907 dye.

Figure 4(a) illustrates the reason for the significant difference between $J_{\text{sc,max}}$ and $J_{\text{sc,max}}^0$ in Fig. 3, namely, the strong absorption by spiro-OMeTAD (and, to a lesser extent, TiO$_2$) at wavelengths relatively close to the absorption maximum of the dye; almost no light at 380 nm is transmitted more than a few hundred nanometers through a device containing only spiro-OMeTAD and TiO2 and no dye. Although the absorption maxima of the D149 and Z907 dyes are at higher wavelengths than this value, these dyes do absorb substantially near 380 nm. Strong absorption by spiro-OMeTAD at this wavelength could therefore lead to significant efficiency losses. The more absorptive D149 dye competes more effectively with spiro-OMeTAD for light than the Z907 dye, resulting in the higher $J_{\text{sc,max}}$ for D149 than for Z907 shown in Fig. 3.

Figure 4(b) shows, as expected, that for light with a wavelength near the absorption maximum of the D149 dye around 530 nm, the distribution of light is nonuniform, with the highest light intensity close to the front of the device. This result shows that, at least for wavelengths where the dye absorbs strongly, it is not optical losses due to the thinness of SDSCs compared with liquid DSCs that limit efficiency. Rather, as discussed above, it is the substantial electrical losses of roughly 40\% across the visible spectrum that largely explain the differing efficiencies of solid-state and
liquid DSCs. Optical losses do occur at long wavelengths far from the absorption maximum, as shown in Fig. 4(c) for 640-nm light, in which, aside from periodic oscillations in the light intensity, the distribution of the light intensity is uniform across the active layer, indicating that much of the incident light is reflected from the metal electrode and from the device as a whole.

Given the incomplete filling of pores near the front of the device by the organic hole conductor in SDSCs, 4.9,29 the strong absorption near the absorption maximum of the dye in this region of the device would suggest a potential electrical loss mechanism in SDSCs, since a large proportion of excitons would be generated in a region where the hole mobility would be reduced. However, it can be seen that the calculated IQE in Fig. 2 for D149 and Z907 is essentially constant with wavelength, indicating that recombination losses do not depend on the light intensity at the front of the device for devices of the thickness studied in this work (~2 μm). Pore filling could pose a problem for thicker devices, and this is an issue that needs to be investigated further.

IV. CONCLUSIONS

In summary, we have used the optical transfer-matrix method and accurately measured optical properties of the various layers in a SDSC to determine the spatial distribution of light in these solar cells and to calculate the external quantum efficiency and short-circuit current of SDSCs for different wavelengths and layer thicknesses. By these means, we have been able to distinguish between electrical and optical losses in these devices. Comparisons with experimental measurements of SDSCs containing either a ruthenium complex termed Z907 or an organic dye termed D149 show that the internal quantum efficiency of both these devices is around 60% across the wavelength spectrum, regardless of the dye, indicating significant electrical losses that are not present in standard liquid DSCs, for which IQE is close to 100%. 26

This result suggests that, although improving light absorption by the dye in SDSCs is an important goal, substantial improvements may be achieved by optimizing electrical characteristics such as charge transfer, separation, and transport. Eliminating these electrical losses could almost double the efficiency of SDSCs. Our calculations also indicate that there are significant optical losses due to absorption by the spiro-OMeTAD and TiO2. The more absorptive D149 dye is shown to perform significantly better than the Z907 dye for all device thicknesses.

ACKNOWLEDGMENTS

This project was supported by the United States Department of Energy under Award No. DE-FG36-08GO18018 and by the UK EPSRC under Grant No. EP/F065884/1.

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