Is there recombination in dye sensitised cells at short circuit?

Piers R. F. Barnes, Assaf Anderson, Sara Koops, Ana Morandeira, James R. Durrant and Brian C. O'Regan,
Department of Chemistry, Imperial College London, London SW7 2AZ, UK. piers.barnes@ic.ac.uk

Abstract

The diffusion length of injected electrons in dye sensitised solar cells (L) derived from incident photon-to-electron conversion efficiency (IPCE) measurements is ~20 µm but >100 µm when derived from photoelectrochemical transient measurements. This suggests a problem exists in the interpretation of the measurements. However, for either value of L, less than 5 % of injected electrons recombine during diffusive transport through a 10 µm thick layer of TiO_2 implying that the largest loss of efficiency after light harvesting is via dye excited state decay prior to injection.

Background

Charge carrier recombination in dye sensitised solar cells is generally considered to be negligible under short circuit operating conditions but photocurrents are often lower than expected. At present the mechanism reducing the photocurrent of typical cells below the theoretically expected value is not clear. The diffusion length, L, quantifies the loss of charge to recombination as photo-injected electrons diffuse through the cell's porous TiO_2 film to the collecting electrode.

Estimates of effective diffusion coefficient, D_n, and recombination lifetime, τ_n, of charge carriers at short circuit, derived from light intensity modulation or transient measurements [1, 2] indicate $L = (D_n \tau_n)^{1/2} \sim 100$ µm. This value substantially exceeds TiO_2 film thicknesses and implies almost no loss to recombination during transport of charge at short circuit despite the IPCE losses is observed in typical cells.

To investigate this apparent discrepancy we have determined L in dye sensitised cells using two independent approaches. The multiple-trapping quasi-static model of the cell [3] states that $L = (D_n \tau_n)^{1/2} = (D_0 \tau_0)^{1/2} = constant$ such that L is independent of electron concentration and position. Thus L determined from the conduction band electron diffusivity and lifetime, D_0 and τ_0, should be consistent with L derived from transient measurements.

The first approach to determine L uses IPCE measurements made on cells of differing thickness illuminated from both the front and back [4]. Additionally the injection efficiency, η_{inj}, of electrons from excited dye molecules in the cell can also be estimated. The second approach uses photoelectrochemical transient measurements to derive D_n and τ_n as a function of total electron concentration and hence L as well as other properties of the cell.

Trapped electrons are assumed not to influence the cell at steady state, so IPCE measurements (corrected for reflection and absorption from the glass and electrolyte phases) can be interpreted in terms of the steady state diffusion equation for conduction band electrons of concentration n_c in the porous TiO_2 film:

$$D_0 \frac{\partial^2 n_c(x)}{\partial x^2} - \frac{n_c(x) - n_{c0}}{\tau_0} + \eta_{inj} G(x) = 0 \tag{1}$$

D_0 and τ_0 are independent of position, x, in the film. $G(x)$ is the generation rate of excited dye molecules in the film, η_{inj} is the efficiency of electron injection from these molecules and n_{c0} is the dark conduction electron concentration.

Expression (1) can be solved analytically to give $n_c(x)$ at short circuit for cells of thickness d with the boundary conditions $n_c(0) = n_{c0}$ and $dn_c(d)/dx = 0$. $G(x) = \alpha I_0 \exp[-(\alpha+\alpha_i) x]$ for illumination from the substrate-electrode (SE) side of the film at $x = 0$ and $G(x) = \alpha I_0 \exp[-(\alpha+\alpha_i)(d-x)]$ for illumination from the electrolyte-electrode (EE) side of the film at $x = d$ where I_0 is the intensity of monochromatic light entering the initial surface of the TiO_2 film, α and α_i are the absorption coefficients of the dye and the iodine on and in the TiO_2 respectively. The IPCE is then given by $[D_0 dn_c(0)/dx]/I_0$, and if α, α_i and d are known the IPCE becomes a function (not written out) of η_{inj} and L. Thus analysis of optical and IPCE data for cells of differing TiO_2 film thickness yields L and η_{inj}. Furthermore a fit to the ratio of the IPCEs for EE and SE illumination gives L alone since the η_{inj} terms cancel.

The time constant of a photocurrent transient decay, τ_j, can be approximately related to the effective diffusion coefficient in the TiO_2 according $D_n = d^2/(2.35 \tau_j)$ [5]. A combination of photovoltage transient decay data and charge extraction data gives τ_n as a function of total electron concentration, n, in the cell. A charge extraction measurement under short circuit operating conditions yields the appropriate value n for τ_n at short circuit used to derive $L = (D_n \tau_n)^{1/2}$.

Experimental

Standard dye-sensitised cells were fabricated using TiO_2 films between 3 and 16 µm thick prepared on fluorine doped tin oxide (FTO) coated glass substrates [2]. The TiO_2 films were treated with $TiCl_4$, then sensitised using N719 dye and filled with an electrolyte composed of MPN, benzimidazole, guanidinum thiocyanate and 50 mM Iodine. The counter electrode was a thin layer of platinum covering an FTO glass substrate, sealed using surlyn and a glass coverslip.

IPCE measurements were made using a shuttered monochromated light source where the intensity was calibrated using a UV-enhanced silicon photodiode. The optical properties of the cells were determined by measuring the transmission of the various cell components in different combinations using a UV-visible spectrometer. Transient photocurrent, photovoltage and charge extraction measurements were made to determine the electron transport time, recombination time and trap state concentration in the cells [2].
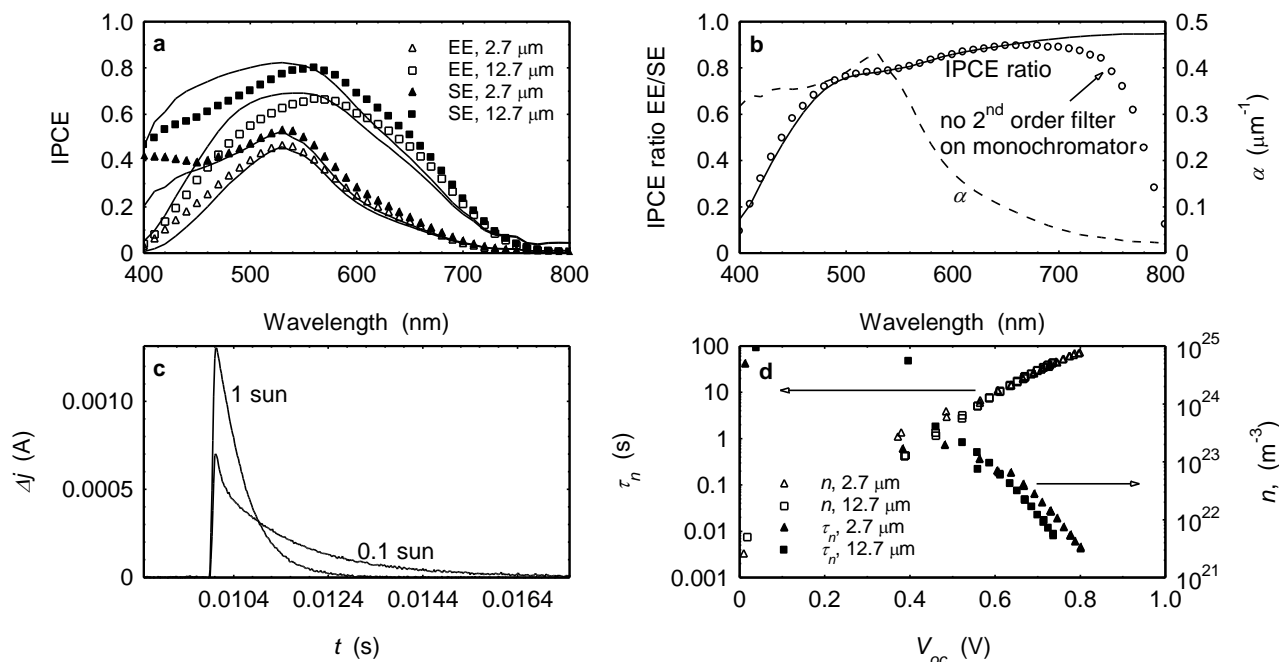
Results and discussion

Figure **a**. *Example IPCE measurements with SE illumination and EE illumination on films of different thickness. Solid lines show modelled IPCE.* **b**. *The ratio of the IPCE measured with EE to SE illumination, the solid curve shows the fit dependent only on L. The example is for a 15.8 μm cell. The absorption coefficient of the dye on TiO_2 is also shown taken from an average of 7 cells of different thickness.* **c**. *Example of short circuit photocurrent transient data for a 2.7 μm cell at different bias light intensities.* **d**. *Example of recombination time and electron concentration against open circuit voltage from transient and charge extraction data.*

The figure shows examples of the optical, IPCE, charge extraction and transient data collected. Curves modelled with two free parameters, L and η_{inj}, fitted simultaneously on 8 IPCE measurements of cells of different thickness are shown in Figure a. The fit yielded $L = 23.4$ μm and $\eta_{inj} = 0.88$. An example fit to the measurement of the IPCE EE/SE illumination ratio is shown in Figure b. The diffusion length fitted to the thicker (7 -16 μm) cells using this technique was 23 ± 11 μm. At one sun SE illumination $L = 23$ μm corresponds to recombination loss of 0.5 % or 4.4 % of the injected electrons at short circuit for cells of 3 and 10 μm thickness respectively.

The transient photocurrent measurements gave $D_n = 5.2 \times 10^{-9}$ m^2 s^{-1} and 1.6×10^{-9} m^2 s^{-1} in the 2.7 μm film under 1 and 0.1 sun illumination respectively and $D_n = 3.4 \times 10^{-8}$ m^2 s^{-1} and 8.6×10^{-9} m^2 s^{-1} in a 12.7 μm film. Due to RC limitation of the measurement of τ_j these values represent minimum effective diffusion coefficients. The transient photovoltages, combined with charge extraction at short circuit measurements allowed appropriate recombination lifetimes to be determined for these conditions. The corresponding values of L were 135 and 100 μm, for the 2.7 μm film at 1 and 0.1 sun, and 210 and 170 μm for the 12.7 μm film at 1 and 0.1 sun respectively; these values correspond to negligible current loss during electron collection at short circuit. Since at short circuit n varies with position in the cell but τ_n is determined for the mean n, these values cannot be considered to have a precise physical meaning however it is clear that they are at least 5 times greater than the equivalent values of diffusion length measured using the IPCE method.

Conclusions

We have shown a substantial difference in the L values derived from IPCE measurements relative to L derived from transient measurements. The transient value of L is consistent with values inferred from previous measurements [1,2] but the difference compared to the L values derived here from IPCE data suggest there may be a problem with the interpretation of the this data or, the application of, or assumptions implicit within, the quasi-static multiple trapping model. However the absolute values of L in both cases do not suggest substantial recombination during collection in most cells; a greater fraction of harvested photons are lost (12%) before the charge injection step.

[1]   Peter, L. M. *J. Phys. Chem. C* **2007,** *111,* 6601-6612
[2]   O'Regan, B. C., Bakker, K., Kroeze, J., Smit, H., Sommeling, P. and Durrant, J. R. *J. Phys. Chem. B.* **2006,** *110,* 17155-1760
[3]   Bisquert, J. and Vikhrenko, V. S. *J. Phys. Chem. B* **2004,** *108*, 2313-2322
[4]   Södergren, S. Hagfeldt, A., Olsson, J. Lindquist, S.-E. *J. Phys. Chem.* **1994**, *98,* 5552-5556
[5]   Van de Lagemaat, J. and Frank, A. J. *J. Phys. Chem. B* **2001,** *105,* 11194-1120