

Non-linear transport and recombination of free electrons in dye sensitized solar cells

Piers R. F. Barnes,* Kati Miettunen, Yiqi Liu, Roger Jiang and Brian C. O'Regan

Department of Physics and Department of Chemistry, Imperial College London, SW7 2AZ, UK. *piers.barnes@imperial.ac.uk

Non-ideal voltage-light intensity behaviour of dye sensitized solar cells (DSSCs) can contribute to a significant loss in fill factor. The nature of this phenomenon remains a topic of debate, and has recently been attributed to sub-linear recombination kinetics of free electrons.¹ In this work we demonstrate that free-electron transport is also non-ideal in a wide range of DSSCs, typically by a similar amount to the apparent non-ideality of recombination. This implies that the observation of non-linear recombination may be primarily due to transport limitations of conducting electrons.

The concentration of electron accepting species in a DSSC's electrolyte is many orders of magnitude greater than the equilibrium concentration of electrons in the depleted TiO₂ nanocrystals that form a high surface area scaffold for adsorbed dye molecules. Thus the TiO₂/Dye/electrolyte composite can be thought of as a p-type effective medium where conducting electrons are the minority carrier transported by diffusion. A consequence of this is that the photovoltage of a DSSC is dominated by variations in the concentration of conducting electrons (n_c) which change the electron quasi-Fermi energy relative to the redox potential of the electrolyte (E_F). The ideality of a DSSC normally refers to an apparent deviation of n_c from a Boltzmann dependence on voltage

$$n_c = N_c e^{\frac{(E_F - E_C)}{mk_B T}} \quad (1)$$

where at open circuit $qV_{oc} = E_F$ and E_C is the conduction band energy relative to the electrolyte redox potential which is normally assumed to be fixed. N_c is the total density of conduction band states, q is the charge on an electron, k_B is Boltzmann's constant and T is the temperature. The factor m parameterises the ideality; in an ideal cell, $m = 1$. In practice virtually all DSSCs show an ideality of $m = 1.05 - 1.9$.

Under open circuit, steady state, conditions the rate of electron injection into the TiO₂ from dyes excited by an incident photon flux ϕ is balanced by the rate of electron recombination (primarily with the acceptor species in the electrolyte).

$$\frac{\phi \eta_{LH} \eta_{inj}}{d} = \frac{n_c}{\tau_0} \quad (2)$$

Here d is the TiO₂ film thickness, η_{LH} and η_{inj} are the light harvesting efficiency and the electron injection efficiency respectively (both assumed to be constant under operating conditions),² and τ_0 is the pseudo-first order conduction electron lifetime (also assumed to be approximately constant). If recombination is linear, then at open circuit we expect $\phi \propto n_c$. From equations 1 and 2 we see that n_c , and consequently the cell photovoltage, V_{oc} , is controlled by recombination. The ideality of a device at open circuit, which we will call m_{rec} , can thus be estimated by measuring V_{oc} at different light intensities (ϕ). Generally this yields a straight line on a linear-log plot and its slope gives m_{rec} (see figure 1a):

$$m_{rec} = \frac{q}{k_B T} \frac{dV_{oc}}{d \ln \phi} \quad (3)$$

The effects discussed herein are illustrated with detailed measurements on two different nanocrystalline TiO₂ DSSCs. The first was sensitised with C106 dye with an iodide/triiodide redox electrolyte. The second is sensitised with HW456 dye with a cobalt based electrolyte. Figure 1a shows measurements of the two cells from which the ideality factor is derived using

equation 3. In both cases m_{rec} is significantly greater than 1. The devices can also be considered as a form of diode where the current density (j) in the dark measured as a function of voltage can be used to estimate m_{rec} with the diode equation:

$$j = j_s \left(e^{\frac{m_{rec} V}{k_B T}} - 1 \right). \quad (4)$$

The dark current corresponds to a 'recombination' current of electrons in the TiO₂ (where the Fermi level $\sim qV$) with holes in the electrolyte. Here j_s is the saturation current density. Figure 2 shows that, after correcting the applied voltage for the series resistance, the values of m_{rec} obtained are similar to the values derived from ϕ vs. V_{oc} in Figure 1a.

Recently Bisquert and Mora-Sero¹ suggested that the observed non-ideality in devices could be explained if free (conduction) electron recombination was effectively sub-linear such that τ_0 in equation 2 was dependent on the conduction band electron concentration: $1/\tau_0 = kn_c^{1-b}$ where k is the recombination rate constant and b is the order of free electron recombination (where typically $b < 1$). In this case the ideality of a device is given by the inverse of the free electron recombination order b such that $m_{rec} = 1/b$ so that sub-linear free electron recombination explains the non-ideal relationship between light intensity and V_{oc} , and Boltzmann statistics of n_c are not violated. This model also explains the observed increases in the electron diffusion length (L_n) with increasing voltage or electron concentration. However the description assumes that the transport of conduction electrons through the TiO₂ is ideal. We now examine approaches to measure the ideality of electron transport to test if this is the case.

In a cell displaying ideal electron transport the diffusive flux of electrons, and thus current, is expected to be linearly proportional to the gradient in conducting electrons at the substrate if the free electron diffusion coefficient (D_0) is constant. We also expect the photocurrent (j_{sc}) to be proportional to the mean concentration of conduction electrons in the device when the efficiency of electron collection (η_{col}) at short circuit is close to 100% given that the concentration at the substrate, $n_c(x=0) \approx 0$:

$$j_{sc} = -qD_0 \frac{dn_c}{dx} \propto n_c \quad (4)$$

where x is the TiO₂ position perpendicular to the substrate.

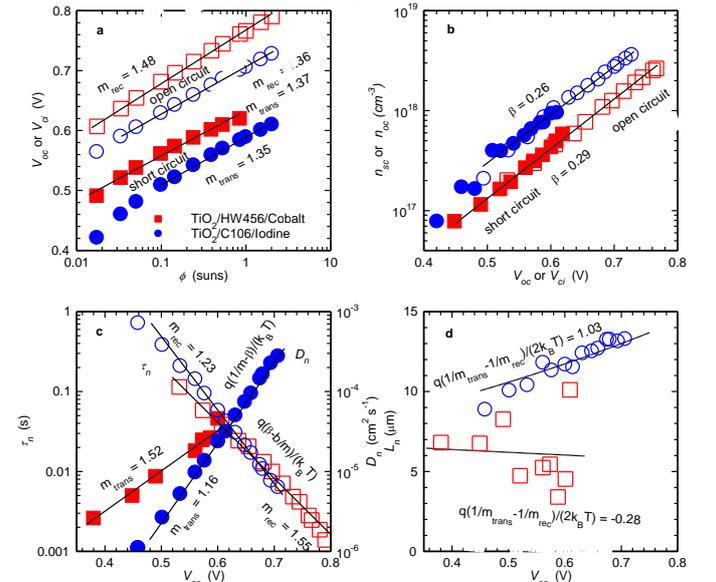


Figure 1. Transient and steady state characteristics of two DSSCs: TiO₂/C106/Iodine (blue circles) and TiO₂/HW456/Cobalt (red squares). **a.** Open symbols: open circuit voltage (V_{oc}) vs. photon flux (ϕ). Closed symbols: current interrupt voltage (V_{ci}) vs. ϕ . **b.** Open symbols: charge extracted from open circuit (n_{oc}) vs. V_{oc} . Closed symbols: charge extracted from short circuit (n_{sc}) vs. V_{ci} . **c.** Open symbols: small perturbation photovoltage relaxation time constants (τ_n) measured at open circuit vs V_{oc} . Closed symbols: small perturbation electron diffusion coefficient (D_n) derived from photovoltage transient (blue circles) and from photocurrent transients (red squares). **d.** Small perturbation electron diffusion length (L_n) plotted vs. V_{oc} .

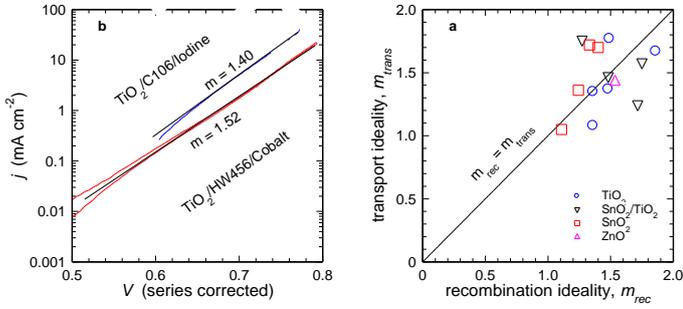


Figure 2. **a.** Exponential sections of the dark current voltage curve in forward bias for the two cells shown in figure 1. **b.** Ideality of transport (m_{trans}) inferred from V_{ci} vs. ϕ plotted against the corresponding ideality of recombination (m_{rec}) inferred from V_{oc} vs. ϕ for a range of different DSSCs. The measurements were made on devices with fabricated using different dyes (N719, C106, TG6, A9, JM3306, HW456 and MsqB), nanocrystalline metal oxide films (TiO₂, SnO₂, ZnO and SnO₂ coated with TiO₂) and electrolytes (I^-/I^+ and Co^{2+} , Co^{3+}).

The average value of n_c in the film required to create the electron concentration gradient for short circuit current collection is associated with an internal photovoltage. The value of this internal photovoltage, or E_F , can be estimated using a current interrupt transient measurement^{3, 4} which yields a plateau voltage, V_{ci} , corresponding to the average n_c . This assertion is confirmed by measuring the total concentration of trapped and free electrons in the device (n_{sc}) at short circuit using charge extraction. When n_{sc} is plotted against V_{ci} the curve is seen closely overlie the curve obtained by plotting the charge extracted at open circuit (n_{oc}) against V_{oc} (see figure 1b). This indicates that the internal voltage in the device measured by current interrupt corresponds to the same concentration of electrons that would be observed at an equivalent open circuit voltage. Since, at short circuit, V_{ci} gives a proxy for n_c (assuming $qV_{ci} = E_F$ in equation 1) the ideality of electron transport, which we will call m_{trans} , can be found by measuring V_{ci} as a function of light intensity (where $\phi \propto j_{sc}$):

$$m_{trans} = \frac{q}{k_B T} \frac{dV_{ci}}{d \ln \phi} \quad (5)$$

The examples of these measurements shown in figure 1a indicate that the non-linearity of electron transport appears to be roughly similar to that observed for recombination; i.e. $m_{trans} \sim m_{rec}$. This suggests that the same effect may influence both processes. Note that transport via localised trapping states cannot easily be invoked to explain the non-linear transport of conducting electrons in the way it is used to explain sub-linear recombination because the density of trapping states appears to be too low for significant transport via inter-trap tunnelling.

The linearity of electron transport and recombination can also be examined using small perturbation transient measurements.⁴ These measurements allow the effective electron diffusion coefficient (D_n) and lifetime (τ_n) to be measured at different voltages or charge concentrations. Figure 1c shows D_n and τ_n measured using small perturbation photovoltage time of flight measurements (which show good agreement with electrochemical impedance spectroscopy).⁴ The values change exponentially with the voltage in the device. This is explained by trap-limited electron transport and recombination since only a tiny fraction of the total charge (n_{oc} or n_{sc}) is in the conduction band of the TiO₂ (n_c).⁵ The majority of the electrons are thought to reside in localised states below the conduction band energy (E_C) and this trapped charge remains in dynamic thermal equilibrium with the conduction band during small perturbation measurements. The exponential distribution of trapped electrons seen in figure 1b (where the slope is described by the temperature dependent parameter β) results in an exponential change in D_n and τ_n as the ratio of free to trapped charge increases with voltage. The following relationships are predicted by this multiple trapping model:^{4, 6}

$$D_n \propto \exp \left[\frac{qV}{k_B T} \left(\frac{1}{m_{trans}} - \beta \right) \right] \quad (6)$$

$$\tau_n \propto \exp \left[\frac{qV}{k_B T} \left(\beta - \frac{1}{m_{rec}} \right) \right] \quad (7)$$

$$L_n \propto \exp \left[\frac{qV}{2k_B T} \left(\frac{1}{m_{trans}} - \frac{1}{m_{rec}} \right) \right] \quad (8)$$

The values of m_{trans} and m_{rec} derived from the data in figure 1c using these expressions show rough agreement with the values derived from the V vs. $\ln(\phi)$ data in figure 1a. The differences between the corresponding values of m_{trans} and m_{rec} also explain the variation in electron diffusion length with voltage since the diffusion length is given by $L_n = (D_n \tau_n)^{1/2}$ (see figure 1d). Note that if $m_{trans} = m_{rec}$ then L_n is constant even when the cell is not ideal. This is almost the case in the cobalt electrolyte cell example presented in figure 1d which shows almost no trend in diffusion length with voltage.

To examine how general these observations of device ideality are, the analysis used to find m_{trans} and m_{rec} illustrated in figure 1a was performed on a wide range of DSSCs. The devices were fabricated using different nanocrystalline films: TiO₂, SnO₂, ZnO and SnO₂ with TiO₂ core shell structures (obtained using a TiCl₄ treatment of the SnO₂ films). The films were sensitised with a range of different dyes, and different electrolytes were also used (see figure 2b caption). Figure 2b shows the ideality determined at short circuit (m_{trans} , equation 5) plotted against the ideality determined at open circuit (m_{rec} , equation 3) for each of the cells. Here the focus is not on the specific differences between the devices but on the spread of ideality values observed. The figure shows the ideality ranges between 1 - 2 for both measurements of the cells. In general transport is not ideal ($m_{trans} > 1$) and there is a loose correlation with m_{rec} such that $m_{trans} \sim m_{rec}$. A similar specific observation was observed for a highly non-ideal cell made using TiO₂ nanotubes by Jennings *et al.*⁷

From this evidence we suggest that the same physical process may be primarily influencing both the transport and recombination of conducting electrons within nanocrystalline semiconducting films, which we parameterise as m . This seems reasonable since we expect that the recombination of electrons will be limited by their transport to a recombination site. We speculate that an additional process could also solely influence recombination in some cases (perhaps mediated by trapping states) as suggested previously¹ which accounts for variations of L_n with voltage, parameterised by the free electron recombination order b . The ideality of transport and recombination can thus be written in these terms:

$$m_{trans} = m \quad (9)$$

$$m_{rec} = m/b \quad (10)$$

The physical nature of m could result from a number of possible causes, for example: varying electron activity,⁷ a non-linear conduction band mobility, interparticle variations of E_C or an unpinning of E_C resulting from changes in the Helmholtz layer. It remains a topic of investigation.

In summary our results suggest that the primary factor influencing the observed ideality of DSSCs (and thus their fill factor) affects the transport of conducting electrons in roughly the same manner as their recombination.

P.B. is grateful to the EPSRC for funding this work.

1. J. Bisquert and I. Mora-Sero, *J. Phys. Chem. Lett.*, 2010, **1**, 450-456.
2. P. R. F. Barnes, A. Y. Anderson, S. E. Koops, J. R. Durrant and B. C. O'Regan, *J. Phys. Chem. C*, 2009, **113**, 1126-1136.
3. G. Boschloo and A. Hagfeldt, *J. Phys. Chem. B*, 2005, **109**, 12093-12098.
4. P. R. F. Barnes, K. Miettunen, X. Li, A. Y. Anderson, T. Bessho, M. Gratzel and B. C. O'Regan, *Advanced Materials*, in preparation.
5. J. Bisquert and V. S. Vikhrenko, *J. Phys. Chem. B*, 2004, **108**, 2313-2322.
6. P. R. F. Barnes, A. Y. Anderson, J. R. Durrant and B. C. O'Regan, *Phys. Chem. Chem. Phys.*, 2011, **13**, 5798-5816.
7. J. R. Jennings, A. Ghicov, L. M. Peter, P. Schmuki and A. B. Walker, *J. Am. Chem. Soc.*, 2008, **130**, 13364-13372.