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On the methods of calculation of the charge collection efficiency for dye sensitized solar cells

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The charge collection efficiency is one of the most critical parameters of photovoltaic devices. In this paper we provide the analysis and comparison between several approaches for the calculation of the collection efficiency for dye-sensitized solar cells. In addition, we point out that although it is reasonable to correlate transit time and recombination lifetime with respect to diffusion length, it is less physical to directly calculate collection efficiency only based on characteristic time constants.

Charge collection efficiency of solar cells, often termed η_{coll} , is of major importance in order to assess the quality of charge collection at short circuit with respect to charge generation in the active layer. The measurement of η_{coll} is quite simple and relies on the ratio of the short circuit current and the total light generated current. When the electron injection efficiency η_{inj} equals unity, η_{coll} can be defined by:

$$\eta_{\text{coll}} = \frac{j_{\text{sc}}}{q\Phi(1 - e^{-\alpha d})} \quad (1)$$

where q is the elementary charge, Φ the incident light intensity, α the absorption coefficient and d the thickness of the active layer.

The underlying limiting processes of the collection efficiency are recombination and diffusion. For dye sensitized solar cells (DSCs), both processes can be characterized respectively by the recombination lifetime (τ_R) and diffusion transit time (τ_{tr}) defined by¹:

$$\tau_R = \left(\frac{\partial U}{\partial n}\right)^{-1} \quad (2)$$

$$\tau_{tr} = \frac{D_n}{d^2} \quad (3)$$

where $U(n)$ and D_n represent the electron recombination rate and the diffusion coefficient for electrons, respectively. τ_R and τ_{tr} are key parameters that permit to assess the quality of the charge collection at the substrate/electrode contact. Indeed, if the transit lifetime is much shorter than the recombination lifetime ($\tau_R/\tau_{tr} \gg 1$), it is equivalent to say that the diffusion length is much larger the device active layer and the cell has an excellent collection efficiency ($\eta_{\text{coll}} \approx 1$). The connection between the

ratio of both lifetime constants and the ratio between diffusion length versus the active layer thickness has already been established by Bisquert²:

$$\frac{\tau_{tr}}{\tau_R} = \frac{R_t}{R_{rec}} = \left(\frac{d}{L_n}\right)^2 \quad (4)$$

In the analysis of DSC it has become very common to calculate these time constants in order to assess the quality of charge collection. Two main methods are usually used to measure τ_R and τ_{tr} : i) τ_R can be measured by IMVS under open circuit (OC) conditions and τ_{tr} can be measured by IMPS under short-circuit (SC) conditions. ii) Another efficient method is Impedance Spectroscopy (IS), which allows one to obtain the recombination resistance R_{rec} and the transport resistance R_t with a consistent Fermi level.

Regarding the relation between the collection efficiency and the time constants, several expressions can be found in the literature, and we discuss in this communication the main approaches that are usually adopted. The following expression is widely used³⁻⁵

$$\eta_{\text{coll},\tau} = 1 - \frac{\tau_{tr}}{\tau_R} \quad (5)$$

Equation (5) is intuitively appealing, based on the idea of the relative probabilities for recombination and collection of a photogenerated electron³. Unfortunately Eq. (5) has not been derived from first principles, and we show below that it is not correct and in fact it is rather inaccurate for the cases of interest. Equation (5) should be valid only under the condition that the cell active layer is thin enough so that the bunch of photo-generated electrons could either recombine or be immediately collected to contribute to j_{sc} . However, in practice, the film thickness (typical value is around 8-10 μm) of DSCs is usually far away from this condition. Therefore, the spatial extension of the semiconductor layer should be taken into account in order to obtain the correct collection efficiency. In fact, at every point of the active layer of a solar cell, charges can either recombine or transit, with a variable probability at every point, due to the variable distance from the contact. From these qualitative considerations it is obvious that eq. (5) is not a useful way to estimate the collection efficiency of DSCs. A quantitative discussion will be made later on.

We mention that attention should be paid to the measurement method of the lifetime constants τ_R and τ_{tr} . Even though IMPS and IMVS methods have been proven to be a powerful tool to explain transport in semiconductors, one should be careful. Indeed it exists a difference in *quasi Fermi levels* (QFL) at OC and SC, which, according to Peter et al.^{6,7} is around 200 meV in DSCs. Given that DSCs are characterized by a large density of traps, a difference in QFL implies a difference in trap dynamic at OC and SC. Since both of $\tau_{R,IMVS}$ and $\tau_{tr,IMPS}$ depend on the trap dynamic, it is consequently meaningless to directly compare these two dynamic time constants. In this case only if including the correction into QFL the comparison between $\tau_{R,IMVS}$ and $\tau_{tr,IMPS}$ is possible. As suggested by Peter, this correction can be done by imposing a different light intensity in order to obtain identical QFLs at SC and OC at the substrate/electrode contact.

The standard way to properly derive the collection efficiency is to apply equation (1), in which j_{sc} can be calculated in two ways. Note that the ensuing considerations only apply to the case of linear recombination. The most direct way is to solve the transport equation under light illumination. Such a derivation has already been done analytically by Södergren et al.⁸ for the case of DSCs with linear recombination. The other method consists in solving the diffusion equation under dark conditions and apply the non-trivial reciprocity theorem of Donolato.⁹ According to this result, for a solar cell with a linear recombination, the short circuit current can be achieved by integrating the product of the generation rate, $G(x)$, and the collection probability P_{coll} through entire film thickness. The latter quantity is given by the ratio of dark carrier concentration in one point $n(x)$ with respect to the total injected charge density at the substrate/electrode contact ($x=0$):

$$P_{coll} = \frac{n(x)}{n(0)} \Big|_{dark} \quad (6)$$

This last relation emphasizes, on the one hand, that in the linear case, the collection probability does not depend on the working conditions of the solar cell: neither on illumination or on bias voltage. On the other hand, P_{coll} is a function of the position x in the active layer. Thereby, it justifies from another point of view the impropriety of correlating collection efficiency with position-independent time constants only, without considering the diffusion transport process.

Using either one or the other method, the resulting collection efficiency at the substrate is given by:

$$\eta_{coll,Ln}^l = \frac{[-L_n \alpha \cosh(\frac{d}{L_n}) + \sinh(\frac{d}{L_n}) + L_n \alpha e^{-\alpha d}] L_n \alpha}{(1 - L_n^2 \alpha^2)(1 - e^{-\alpha d}) \cosh(\frac{d}{L_n})} \quad (7)$$

When $L_n \gg d$ (i.e. when $\eta_{coll} \approx 1$), a series expansion of eq. (7), assuming that $\alpha d \gg 1$, leads to:

$$\eta_{coll,Ln}^l \approx 1 - \frac{1}{\alpha d} \left(\frac{d}{L}\right)^2 = 1 - \frac{1}{\alpha d} \frac{\tau_{tr}}{\tau_R} \quad (8)$$

Note that for DSCs, recombination is often non-linear and is of the type¹⁰ $U(n) = k_r(n^\beta - n_0^\beta)$. In this case eq. (7) is not valid and one should solve numerically the continuity equation for electrons¹¹.

In order to compare both collection efficiencies, $\eta_{coll,\tau}$ and $\eta_{coll,Ln}^l$, based on the valid relation shown by eq. (4), one could link the ratio τ_{tr}/τ_R to d/L_n by inserting eq. (4) into eq. (5):

$$\eta_{coll,\tau} = 1 - \left(\frac{d}{L_n}\right)^2 \quad (9)$$

However, even in this case, since we have already clarified the incorrectness of eq. (5), finally what we get in eq. (9) is still problematic. In addition, from equation (9), it can be noted that $\eta_{coll,\tau}$ can only work for $d \leq L_n$ case, which is another limit of this equation. In particular it should be noted that in the case $d=L_n$, which has been observed and discussed several times^{7,12-14}, eq. (9) leads to $\eta_{coll,\tau} = 0$. This indicates that eq. (9) does not describe properly the collection efficiency for the regular DSC devices.

In Figure 1 we provide the comparison between the different collection efficiencies obtained from eq. (5), namely $\eta_{coll,\tau}$ and eq. (7), $\eta_{coll,Ln}^l$, in the linear case, by plotting the collection efficiency as a function of the ratio L_n/d . We also provide an example of collection efficiency in the non-linear case, $\eta_{coll,Ln}^{nl}$. It can first be remarked that the lower the diffusion length with regard to the active layer length, the larger the discrepancy between $\eta_{coll,\tau}$ and both $\eta_{coll,Ln}^l$ and $\eta_{coll,Ln}^{nl}$. This discrepancy is even higher in the case of the non-linear recombination since the recombination rate is lower in comparison to the linear case. When $L_n \gg d$, one should be tempted to say that eq. (5) is valid. However eq. (8) clearly shows that eq. (9) (and consequently eq. (5)) is not valid even when $\eta_{coll} \approx 1$.

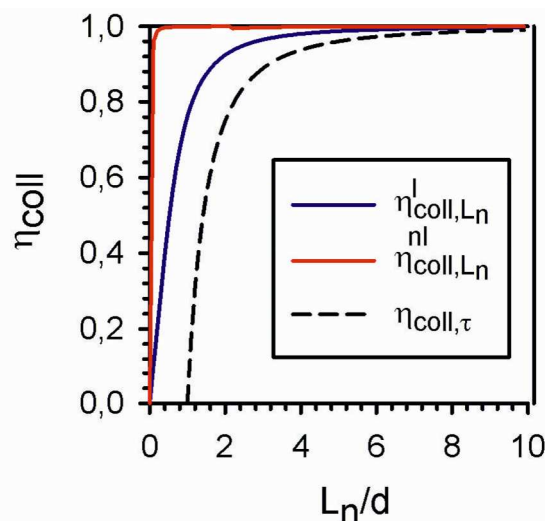


Fig. 1 Comparison of the collection efficiency $\eta_{coll,\tau}$ often found in the literature (dashed lines) and the one calculated from first principles by Södergren et al. in the linear case, $\eta_{coll,Ln}^l$ (blue solid line) and the one obtained in a non-linear case, $\eta_{coll,Ln}^{nl}$ (red solid line). Parameter of the simulation: $d = 8\mu m$, illumination rate $G(x) = \alpha \Phi_0 \exp(-\alpha x)$ with $\alpha = 10^3 cm^{-1}$, $\Phi_0 = 5 \times 10^{16} cm^{-3} s^{-1}$, non-linear recombination rate: $U(n) = k_r(n^\beta - n_0^\beta)$ with $k_r = 10^2 s^{-1}$, $n_0 = 10^{15} cm^{-3}$, $\beta = 0.85$.

In conclusion we have shown that the expression for the collection efficiency often used in the literature has little accuracy to properly characterize charge collection efficiency in DSCs. This formula is all the more incorrect has the non-linearity of the

recombination processes increases. Therefore, it confirms once again that the expression derived from the resolution of the diffusion-recombination transport equation, either directly or indirectly via reciprocity theorem in the linear case or by numerical means in the non-linear case should be regarded as the only acceptable approach for the calculation of the collection efficiency.

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Notes and references

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- 1 J. Bisquert, F. Fabregat-Santiago, I. Mora-Seró, G. Garcia-Belmonte, and S. Giménez, *J. Phys. Chem. C*, 2009, **113**, 17278.
- 2 J. Bisquert, *J. Phys. Chem. B*, 2002, **106**, 325.
- 3 G. Schlichthorl, N.G. Park and A. J. Frank, *J. Phys. Chem. B*, 1999, **103**, 782.
- 4 J. V. D. Lagemaat, N. G. Park and A. J. Frank, *J. Phys. Chem. B*, 2000, **104**, 2044.
- 5 P. T. Hsiao, Y. L. Tung and H. Teng, *J. Phys. Chem. C*, 2010, **114**, 6762.
- 6 H. K. Dunn and L. M. Peter, *J. Phys. Chem. C*, 2009, **113**, 4726.
- 7 H. Wang, and L. M. Peter, *J. Phys. Chem. C*, 2009, **113**, 18125.
- 8 S. Södergren, A. Hagfeldt, J. Olsson and S-E Lindquist, *J. Phys. Chem.*, 1994, **98**, 5552.
- 9 C. Donolato, *Appl. Phys. Lett.*, 1984, **46**, 270.
- 10 J. Bisquert and I. Mora-Seró, *J. Phys. Chem. Lett.*, 2010, **1**, 450.
- 11 J. A. Anta, J. Idígoras, E. Guillén, J. Villanueva-Cab, H. J. Mandujano-Ramirez, G. Oskam, L. Pellejà and E. Palomares, *Phys. Chem. Chem. Phys.*, 2012, **14**, 10285.
- 12 M. Wang, P. Chen, R. Humphry-Baker, S. M. Zakeeruddin and M. Grätzel, *Chem. Phys. Chem.*, 2009, **10**, 290.
- 13 P. R. F. Barnes, A. Y. Anderson, J. R. Durrant and B. C. O'Regan *Phys. Chem. Chem. Phys.*, 2011, **13**, 5798.
- 14 J. R. Jennings, Y. Liu, F. Safari-Alamuti and Q. Wang, *J. Phys. Chem. C*, 2012, **116**, 1556.

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