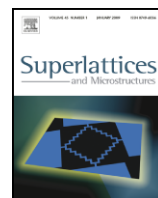




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Analysis and simulation of incident photon to current efficiency in dye sensitized solar cells

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ABSTRACT

Conversion of solar energy into electricity is a challenging issue of today's renewable energy. Electrochemical dye solar cells (DSC), based on nanostructured TiO_2 particles are a very promising class of photovoltaic devices [6]. The mechanism beyond the conversion of the light is quite different from any other solid state solar cell, resulting from the interplay of a fine tuning of the energy levels of the cell components and a delicate fabrication process. This complexity needs a reliable transport model, able to catch the device as a whole and applicable to experimental set up. We developed an extension of TiberCAD [7] code to simulate such kind of devices and compared the calculation with incident photon to current efficiency (IPCE) measurements.

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1. Introduction

Dye solar cells (DSC) are based on a thin layer of TiO_2 nanoparticles (diameter 20 nm) covered with a monolayer of light absorbing molecules. This system is embedded in a liquid electrolyte solution containing a redox pair (Fig. 1). Essentially, a DSC is made of two main regions: the mesoporous photoanode wetted with the electrolyte that penetrates in the interstitial room, and the bulk electrolyte. This compound is sandwiched between two supporting glass layers covered by transparent conductive oxide (TCO); at the cathode is sputtered an additional layer of platinum, acting as a catalyst for the redox reaction. Despite big efforts made in finding a new suitable class of organic dyes, the best performance is obtained with Ru-based organic complexes. The standard redox pair is I^-/I_3^- , but there are promising performances obtained with ionic liquids.

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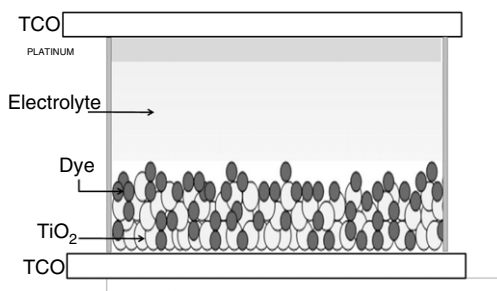


Fig. 1. Scheme of a Dye Solar Cell.

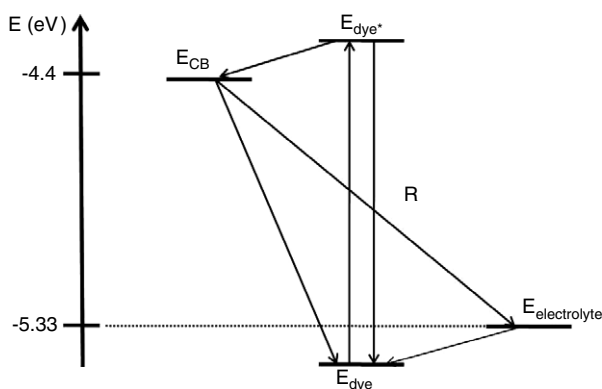


Fig. 2. Energy levels and functioning of a DSC.

Once the light reaches the dye active layer, there may occur a HOMO–LUMO electron transition (Fig. 2). Here, the excited electron can be transferred into the conduction band of the TiO_2 where electrons can percolate up to the anode and be collected. The ionized dye is neutralized by the oxidation of the iodide, while the reduction of triiodide occurs at the cathode. The I^-/I_3^- couple redox reaction is the following:



The driving force moving the redox ions is the concentration gradient produced under illumination. It is worth to notice that there is no chemical modification of any of the components of the cell. However, electron loss reactions occur in the cell, competing with the desired reactions (Fig. 2): electron injection can be lowered by the relaxation of the excited molecule into its ground state, or electron collection at the anode may be reduced by the neutralization of the dye with a TiO_2 electron. Conduction band electrons may also be captured by the oxidized species (triiodide) of the electrolyte. The latter one, labeled as R in Fig. 2 is the most relevant dark current occurring in the cell, as it comes out comparing all the rate constants of these processes [1,2]. In order to better understand the role played by the recombination processes in terms of cell performances, we compare simulation with experiment.

2. Model

We model our cell as a 1D pseudo-homogenous medium, where all the components (TiO_2 , dye, electrolyte) are intermixed. The model treats the four charge carriers (electron, iodide, triiodide and cation), coupled by the Poisson equation for the electrostatic potential. Even if the net current deriving

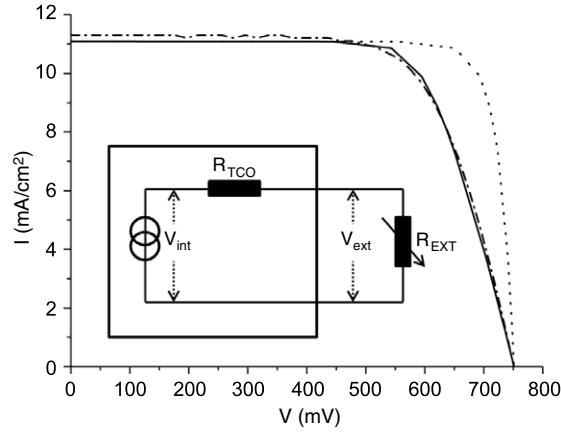


Fig. 3. I – V characteristics for the experimental (long dash), ideal (short dash) and realistic model of the cell (continue). The inset shows the equivalent circuit, where R_{TCO} is the sheet resistance, R_{EXT} is the external load, and the square delimitates the cell area.

from the cation is zero, it must be considered to achieve charge neutrality. The dynamics of all carriers is described by a set of Drift Diffusion equation coupled to continuity equation:

$$\nabla \cdot (\mu_e n_e \nabla \phi_e) = (R - G) \quad (2)$$

$$\nabla \cdot (\mu_{I^-} n_{I^-} \nabla \phi_{I^-}) = -\frac{3}{2}(R - G) \quad (3)$$

$$\nabla \cdot (\mu_{I_3^-} n_{I_3^-} \nabla \phi_{I_3^-}) = \frac{1}{2}(R - G) \quad (4)$$

$$\nabla \cdot (\mu_c n_c \nabla \phi_c) = 0 \quad (5)$$

where ϕ_x is the electrochemical potential, μ_x is the mobility and n_x is the carrier density of the species x .

Besides imposing mass and charge conservation inside the cell, we must define some further constraints for the current at the electrodes. At the anode, we impose no ionic current and ohmic contact for the electrons, while at the cathode we assume no electrons flowing and a splitting of the current following the redox reaction (Eq. (1)).

In the limit of the approximations of this model [2], we can show how to fit an experimental I – V characteristics of a standard DSC made in our laboratories.

2.1. Fit an I – V characteristic

Our model is very sensitive to electron related parameters variations: mobility and recombination constant rate [3]. Fine tuning these two values, makes it possible to fit the experimental I – V curve of a 10 μ m thick standard DSC measured under sun simulator at AM 1.5 G conditioning. To fabricate this standard cell, we use N719 [RuL2(NCS)2]: 2 TBA (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA = tetra-*n*-butylammonium) as dye, and a solution of I^-/I_3^- in a 3-methoxypropionitrile solution as electrolyte (both purchased by DyeSol). Fig. 3 shows a comparison between the experimental and the calculated curve. The calculation well simulates the J_{sc} and V_{oc} values, while the slope of the curve can be obtained by correcting the output data with the resistance of the TCO. Actually, the latter is not considered by the model, but analysing the equivalent circuit we can post process the calculation obtaining a good fit with experimental curve with a R_{TCO} of 10 Ω/cm^2 . This value is in a reasonable agreement with the experimental value of 8 Ω/cm^2 for the conductive glass. All the parameters of the cell were collected from the literature [2], apart for the mobility of electrons ($\mu_e = 0.8 \text{ cm}^2/\text{V s}$) and the recombination constant ($k_e = 10^3 \text{ s}^{-1}$) resulting from the fitting procedure. However, the values

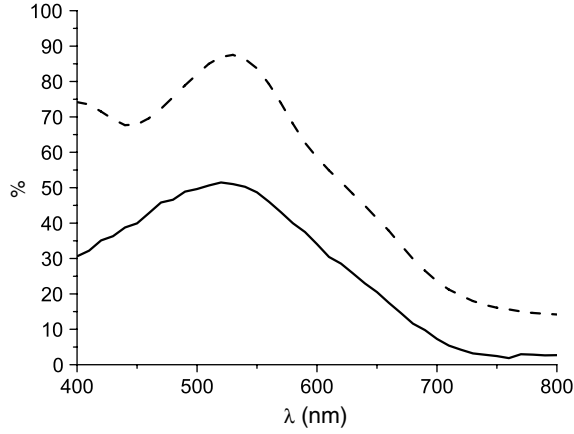


Fig. 4. IPCE measurements (continue) and light harvesting efficiency (dashed) of a standard DSC.

are still in the experimental range. The exact mobility and recombination rate severely depend on the quality of the titanium oxide paste, the sintering of the nanoparticles and on the TiO_2 /electrolyte interface; therefore, it is very challenging to get the correct values.

3. Application to incident photon to current efficiency

In order to gain the limitations and the range of use of the model, we applied our calculation to the experimental measurements of incident photon to current efficiency (IPCE). It measures the spectral response of the cell, containing information on quantum efficiencies of the photocurrent generation (Fig. 4). In particular, IPCE can be factorized into three terms [4]:

$$\eta_{\text{IPCE}}(\lambda) = \frac{J_{\text{sc}}(\lambda)}{e\Phi(\lambda)} = \eta_{\text{LH}}(\lambda)\eta_{\text{INJ}}(\lambda)\eta_{\text{COL}}(\lambda). \quad (6)$$

Following each step of conversion, η_{LH} is the efficiency of the cell in harvesting light, therefore, it is related to the ability of the dye in catching photons. η_{INJ} quantifies the charge transfer from the molecule to the conduction band of TiO_2 . Finally, the collection efficiency η_{COL} is the amount of electrons that effectively reach the anode, avoiding recombination. We calculated the latter term and we focused on the influence of recombination rate on the collection efficiency (Fig. 5). The drop of η_{COL} can be explained by plotting the recombination profile inside the cell (Fig. 6): at very high rate values, recombination follows the generation profile, showing that once an electron reaches TiO_2 it is immediately lost. We measured η_{LH} (Fig. 4) considering the following expression:

$$\eta_{\text{LH}}(\lambda) = T_{\text{TCO}}(\lambda)[1 - R(\lambda, d)] \frac{\alpha_{\text{D}}(\lambda, d)}{\alpha(\lambda, d)} (1 - e^{-\alpha(\lambda, d)d}) \quad (7)$$

where α and α_{D} are the dye and total absorption coefficients and d is the TiO_2 thickness. Following the approach introduced by Tachibana [5], we estimated η_{LH} based on the IPCE measurements obtained with photoelectrode illumination. Spectral reflectance (R) and transmittance (T) were measured with a Shimadzu UV-2550 double blazed grating, double monochromator, UV-vis spectrometer coupled with an external 70 mm diameter integrating sphere (Shimadzu MPC-2200). Solar cell η_{IPCE} was measured at short circuit condition using a computerized setup consisting of a xenon arc lamp (150 W Xe OF-Newport Model 70612) coupled to a 1/8 m monochromator (Cornerstone 130), a Keithley 2400 source meter. The measurements were taken in the absence of bias light with the monochromatic light incident on the cell through a $5 \times 5 \text{ mm}^2$ aperture.

Finally, we can give an estimation of η_{INJ} of the cell we fitted the I - V characteristics, and this value is 50%. This poor injection can be ascribed to a bad chemisorption of the dye onto TiO_2 particles, underlining the criticality of the dipping step during the fabrication process.

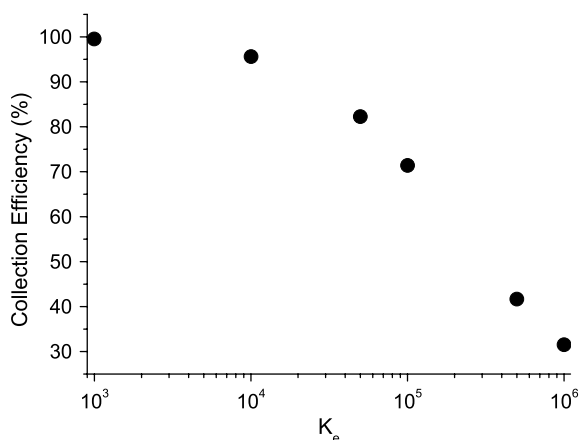


Fig. 5. Electron collection efficiency at the anode, varying recombination constant rate k_e (s^{-1}).

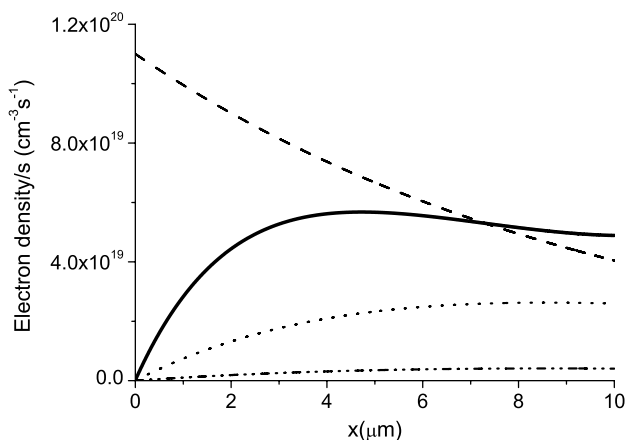


Fig. 6. Generation (dashed-line) and recombination profile varying recombination rate constant $k_e = 10^6 s^{-1}$ (continue), $k_e = 10^5 s^{-1}$ (dot), $k_e = 10^4 s^{-1}$ (dash-dot).

4. Conclusion

We developed a 1D model to simulate the features of a DSC in the framework of TiberCAD. By varying the simulation parameters, we were able to fit an experimental I – V curve of a cell fabricated in our laboratories, taking into account the losses due to the sheet resistance. We focused on the role of the recombination rate in collection efficiency, calculating the generation–recombination profiles in the cell. We applied our model to the IPCE measurements, and combining the simulation results to the experimental response we obtained an estimation of the electron injection efficiency in a DSC.

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