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MULTI-SCALE SIMULATIONS OF DYE SENSITIZED SOLAR CELL

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Abstract
With a few exceptions, Dye-Sensitized Solar Cells (DSSC) simulations based on models with proven accuracy at unique rank level, do not compare well with the experiment. In this paper we propose a three scale level model of DSSC, with individual models in a bottom-up hierarchy connection. Results of numerical simulations focused on the calibration of the individual models are reported.
Keywords: Dye-Sensitized Solar Cells; Multi-scale modeling; Numerical simulation;

1. Introduction

Dye-Sensitized Solar Cells (DSSC) [1] is a blend of multi-scale structured materials (figure 1). Thus, the conversion efficiency is controlled by physical processes at different extent: electron diffusion takes place in a micron sized pseudo-homogenous semiconductor media, charge recombination is a process on a mezoscopic scale while electron injection from excited dye to semiconductor is a quantum chemistry reaction at Ångström scale.

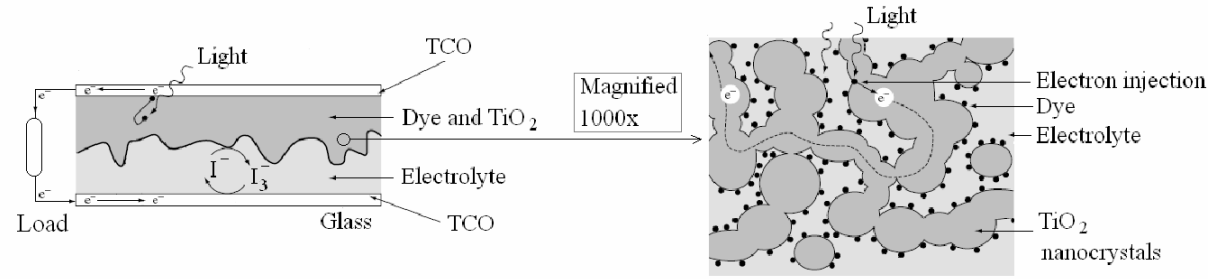

Figure 1. DSSC structure (left), 1000x magnified mezoporous TiO_2 electrode (right)

In this paper we present a three level model for DSSC bottom – up hierarchy connected, as a more accurate alternative to conventional modeling. Results of the individual models testing are presented.

2. DSSC modeling

The Shockley equivalent model of a p-n junction can be applied to a lot of DSSC devices [2]:

$$J = J_{SC}\left[1 - \text{ext}\left(\frac{e\left(V - V_{0C}\right)}{mk_B T}\right)\right] \quad (1)$$

J_{SC} is shortcut current density, V_{0C} is the open circuit voltage and m is the diode factor. But, the physical processes in DSSC are fundamentally dissimilar from the ones in a p-n junction. The model establishes a blurred relationship between (1) p-n equivalent circuit and physical phenomena in DSSC. The fact that results compare well with experiment for several DSSC may originate from the formal equivalence of Shockley ideal solar cell equation and the natural photosynthetic equation:

$$K = K_L - K_0\left(\frac{e\Delta\mu}{k_B T} - 1\right) \quad (2)$$

Equation (2) is derived in [3] assuming a three level quantum system for artificial photosynthesis in analogy with red bacteria natural process. K has the signification of reaction rate: K_L and K_0 correspond to saturation current and photocurrent. Such equivalent circuit models of DSSC are useful in association with experimental approach for finding empirical values in electron kinetic describing [4], [5].

Since DSSC enabled entities at different dimensional scale, the construction of a global model able to correlate the DSSC efficiency with structural parameters is expected in a multilevel modeling approach. In our nanostructure solar cell simulator NANOPV -under development- the DDSC model is incorporated in three steps bottom-up hierarchy in the physical phenomena order logic. First at nano-scale, the electron passing from excited state of dye molecule into TiO_2 semiconductor is accounted as movement on piecewise constant potential, modeled via transfer matrix approach [6]. We note that electron transfer is a delicate subject in quantum chemistry.

The transport coefficients are determined by processes which take place at mesoscopic scale. We chose a Monte Carlo (MC) method for simulating recombination in the TiO_2 electrode and computing the lifetime of photo-generated electrons as a parameter for macroscopic transport equation. The physical model is adopted from [2]. The electron transport consists of a series of jumps between the tail states system of the TIO_2 model that is close to amorphous semiconductor description. The semiconductor electrode is assumed as a pseudo-homogenous media, modeled as a cubic lattice, every node being an electron trap. MC simulation procedure is summarized as follows: The electron in an occupied node decays statistically after a time related to the trap energy (depth) – which is randomized. In the event of decay, the electron attempts a move to a first-neighbor node. It is first verified whether the

place is free. If YES the electron moves. The 3-D system is defined by imposing appropriate periodic boundary condition.

At microscopic level the electron diffusion is described assuming the superposition of semiconductor matrix and electrolyte. The diffusion equation read [7]:

$$i_1 = \varepsilon \mu_n n \frac{d\varepsilon_F}{dx} \; ; \qquad i_2 = \frac{2\varepsilon(\mu_3 - 3\mu_1)}{2 + \ln\gamma} C_3 \frac{d\mu}{dx} \tag{3}$$

$$\frac{di_1}{dx} = -eI\alpha e^{-\alpha x} + ef_{rec} \; ; \qquad \frac{di_1}{dx} + \frac{di_2}{dx} = 0 \tag{4}$$

Here the i_1 and i_2 denote the currents in solid matrix and electrolyte, respectively. n is the electrons density in the semiconductor matrix, ε_F is the cuasi -Fermi level also in the semiconductor matrix. C_3 is the ions concentration in solution. μ with index n, 1 or 3 is the electron mobility, ions I^- and ions I_3^-, respectively. ε is an empirical correction coefficient, α is the light absorption coefficient of dye molecules and I is the light intensity.

3. DSSC as part of NANOPV simulator

For the moment, a nanostructure solar cell simulator, named NANOPV, is under development and testing. It is focused on relating efficiency to geometrical and structural properties of classical p-n junction, quantum wells and dye sensitized solar cells.

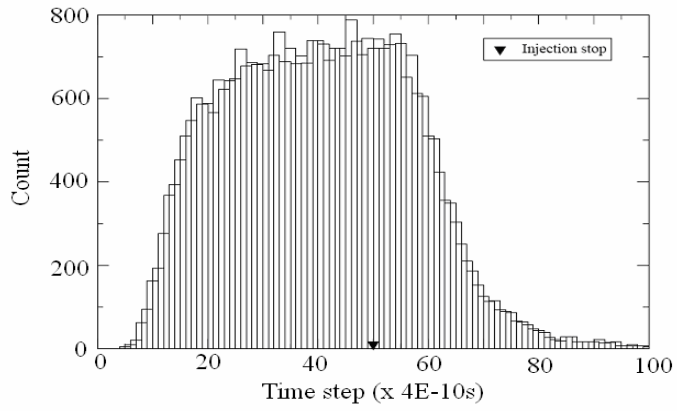

Figure 2. Monte-Carlo simulation of electronic transport. Charge carrier injection starts with the first step and stops at 50. Charge carriers arriving at the output electrode are counted.

This paper refers to DSSC modeling only. Basis of the transfer matrix method used at nanoscale length is acknowledged in our paper [6]. Diffusion at macroscopic scale, equations (3 - 4) with appropriate boundary conditions, are implemented numerically using a finite difference scheme. At mezoscopic scale, a 3-D Monte Carlo simulation program has been developed and tested under intuitive assumptions. Periodic boundary conditions are imposed on two dimensions, while along the third it is terminated with a transparent conductive oxyde

electrode (TCO) where the arriving charge carriers are extracted – and counted. Random numbers are used to simulate statistical decays (detrappings) and random walks as previously stated [2]. In Figure 2 we tested a.) starting carrier injection and output saturation and b.) stopping injection, carrier depletion. Both processes follow exponential laws, the shape of which is perfectly visible in the figure.

4. Conclusions

In this paper we report a three dimensional level DSSC simulator. We are giving more attention to the mesoscopic scale, where we use MC simulation for estimating parameters needed in the microscopic scale simulation.

Acknowledgements

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