Physics based simulation of Dye solar cells

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***Abstract*—Dye sensitized solar cells (DSCs) are interesting candidates for providing a renewable, cost efficient energy source with low environmental impact. Although DSCs are very close to be commercialized, many issues still need to be addressed. Part of the problem is related to the lack of a reliable and consistent simulator able to catch the physics underlying the functioning of the cell. The need of a simulator and modelling tool is particularly important for the engineering of the cell and its optimization. Among the different parts composing a DSC the relevance of the semiconductor titanium oxide (TiO_2) layer can hardly be underestimated. In particular, the physics at the interface between TiO_2 and the electrolyte has a wide impact over the entire device because is the main source of recombination.**

We present a simulation module within the TiberCAD software package designed for the simulation of DSCs in 1, 2 and 3 dimensions. The tool allows to study the impact of material parameters and device geometry on cell performance.

I. Introduction

Recently, solar cells have been gaining increasing attention as a possible technological solution to improve energy production whilst reducing environmental impact. While the majority of the market is still dominated by first generation solar cells based on single crystal or poly-crystalline silicon, third generation cells are arousing much interest for their ability to achieve high efficiency or low production cost. In particular, dye sensitized solar cells (DSCs) [1] have gained much attention due to simple technology and low cost. Moreover, their cell setup allows for innovative device structures, such as flexible devices and integration with building facade windows.

A DSC is fundamentally an electrochemical device, consisting of a mesoporous semiconductor such as titanium oxide (TiO_2) wetted with a photoactive dye and plunged into a liquid electrolyte (Fig.1). The mesoporous TiO_2 is made of nanoparticles sintered together to form a connected network. This titania paste is deposited onto a transparent conductive oxide (TCO), which constitutes the photoanode. The surface of the mesoporous TiO_2 is covered with a monolayer of photoactive molecules, the dye, by chemisorption. The large effective area of the mesoporous phase allows for a high density of dye, leading to efficient light harvesting. The electrolyte usually contains a iodide/triiodide (I^-/I_3^-) redox pair, I^- being the reducer and I_3^- the oxidant. The cell is closed by a counter electrode formed by TCO covered with a thin layer of platinum in contact with the electrolyte acting as catalyst.

The light-to-electricity conversion is working as follows. First, a photon is absorbed by a dye molecule. Then, the excited electron is transferred to the conduction band of the TiO_2 by a fast process, ionizing the dye. The ionized dye is finally regenerated by the electrolyte. This last process changes the ratio of the redox pair concentrations at the TiO_2/electrolyte surface, leading to concentration gradients that push the triiodide towards the platinum cathode. There the triiodide oxides to iodide, taking two electrons from the cathode. There is no permanent chemical reaction in the entire cycle that is completely reversible allowing for a long lifespan of the device.

The splitting of the photogenerated exciton on the dye is very fast, suppressing almost completely recombination processes within the dye or with the electrolyte. However, due to the mesoporous structure, the transport of the electrons injected into the TiO_2 towards the anode is dominated by percolation and is therefore very slow. For this reason recombination mediated by surface traps at the nanoparticle surface is an important issue although the recombination time is relatively long ($\tilde{1}$ ms). The TiO_2 plays so a fundamental role inside the device under many aspects: on one side it is the substrate for the dye, it controls the energy alignment of the excited state of the dye which eventually controls the charge transfer and it is the main source of electron recombination.

II. Simulation model

The DSC simulation model implemented in TiberCAD uses the drift-diffusion approximation to describe carrier transport in the cell [2], [3]. Five carriers are needed to describe a DSC, namely electrons (in the TiO_2), iodide, triiodide, and cations. The cations are needed for charge neutrality in the electrolyte, although they do not participate in the electrochemical processes. The complete model describing the cell reads as follows:

$$\nabla(\mu_e n_e \nabla\phi_e) = G - R \quad (1)$$

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

$$\nabla(\mu_{I_3^-} n_{I_3^-} \nabla\phi_{I_3^-}) = \frac{1}{2}(G - R) \quad (3)$$

$$\nabla(\mu_c n_c \nabla\phi_c) = 0 \quad (4)$$

$$\nabla(\varepsilon\nabla\varphi) = -q\big[n_c + N_D^+ - n_I - n_{I_3^-} - (n_e - \bar{n}_e)\big] \quad (5)$$

Here, μ_α, n_α and ϕ_α are the mobility, the density and the electro-chemical potential of the particle α. G is the electron

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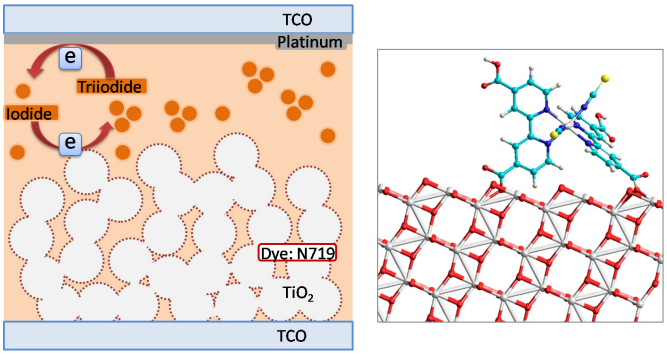

Fig. 1: Scheme of a DSC. On the bottom the TiO_2 (white circles) with the attached dyes (red spots). In the space between the two conductive oxide (TCO) the redox reaction Iodide/Triiodide is shown. On the right we present an atomistic calculation of N719 dye chemisorberd onto a (101) TiO_2 anatase surface.

generation term due to illumination, and R is the recombination rate. φ is the electrostatic potential, and N_D^+ is the density of ionized dyes, given by the generation rate G divided by the dye regeneration rate. For each carrier we assume local thermal equilibrium, and we assume the TiO_2 to be non-degenerate so we can write all particle densities using Boltzmann statistics as $n_\alpha = \bar{n}_\alpha \exp(\pm\frac{q\varphi - q\phi_\alpha}{k_B T})$, where the barred quantities are the densities in thermodynamic equilibrium (dark condition and no external bias applied).

The local generation rate G is related to the photon flux and the absorption in the active TiO_2. It is calculated considering the absorption spectrum of the dye used for the DSCs (usually a Ruthenium complex called N719, Fig.1, right inset) and using the spectral power flux of the illuminating source (standard solar illumination at AM 1.5 G of 100 mW/cm^2).

III. Simulation Examples

We show two examples of simulations performed using the TiberCAD software. In the first example we investigate the influence of the roughness of the TiO_2 on cell efficiency. Fig. 2 shows the three structures simulated. From the simulated IV curves (Fig. 3) we observe a drop of efficiency from 7.9 % to 7.24 %.This drop is due to a reduction of overall photogeneration, provoked by the roughness of the TiO_2 layer.

As a second example, we show a simulation of an exotic cell geometry as proposed in [4]. In this case, a DSC is constructed radially around an optical fiber (Fig. 4). The simulated cell has an efficiency of 6 %.

In both examples, simulations can contribute substantially to the understanding an optimization of the cell structures.

References

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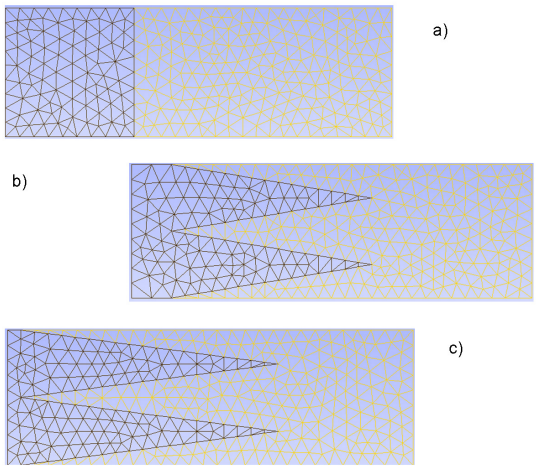

Fig. 2: Three simulated cell structures with different roughness (dark gr

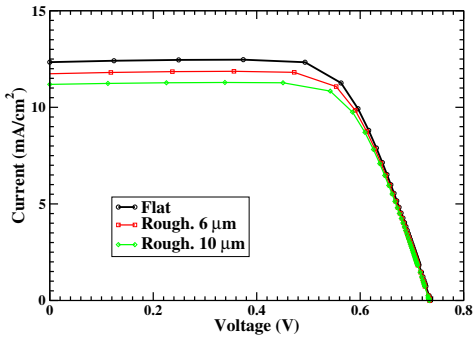

Fig. 3: The simulated IV characteristics for the three structures with different roughness.

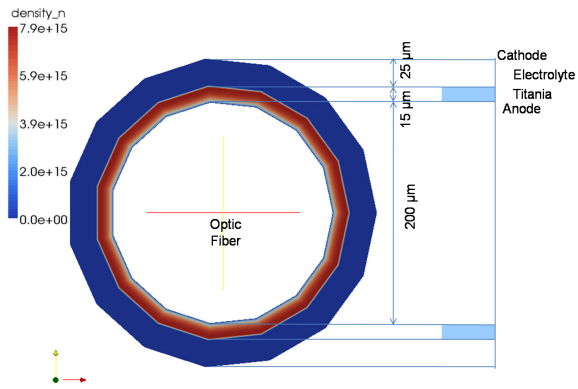

Fig. 4: A radial DSC. The cell is built around an optic fiber. The picture shows the electron density at short-circuit.