

Development and Application of Multiscale Simulator for Dye-Sensitized Solar Cells

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1. Introduction

Dye-Sensitized Solar Cells (DSSC) have been extensively studied since O'Regan and Grätzel [1]. Features of DSSC are low-cost production, wide variety of designs, independence of installation sites, etc. DSSCs are regarded by many as the next-generation solar cells. However, their maximum conversion efficiency is only about 11% [1]; therefore, further research and development effort is necessary to achieve higher conversion efficiencies.

To increase the conversion efficiency, which is determined by the short-circuit current, the TiO₂ porous structure of the dye-adsorbed semiconductor layer needs improved electron diffusivity. Moreover, all excited electrons must be extracted at the conductive electrode. Since experimental studies are heuristic, it is important to perform computer simulations to obtain insights regarding the properties and performance of the microstructure.

For this study, we developed a multi-scale simulator for DSSC devices. This simulator links the micro- to the macro-scale. The micro-scale simulation gives solid state properties and the electron state through quantum chemical calculations. The meso-scale simulation gives the electron diffusivity in complex porous structures. This was developed in a previous study. The macro-scale simulation gives the current-voltage characteristics for DSSC devices. The meso-scale simulator for the electron diffusion processes in TiO₂ complex, porous structures has been built-in the macro-scale simulator for the current-voltage characteristics of DSSC using a three-dimensional porous structure simulator [2,3].

2. Methods

Construction of TiO₂ porous structure model

As the basic unit, we constructed the TiO₂ porous structure model using the three-dimensional porous structure simulator [3] (Fig. 1). This simulator constructs models of irregular porous structures based on an original overlap-allowed particle packing method.

Electron Diffusion Simulation

We performed the electron diffusion simulation to investigate the influences of the porosity and the overlap ratio of TiO₂ particles on the electron diffusion properties

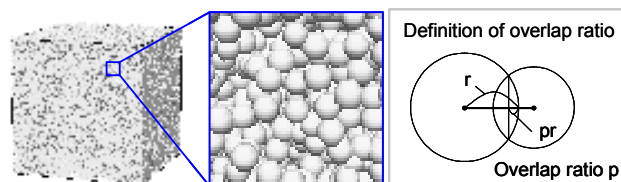


Fig. 1 TiO₂ porous structure model.

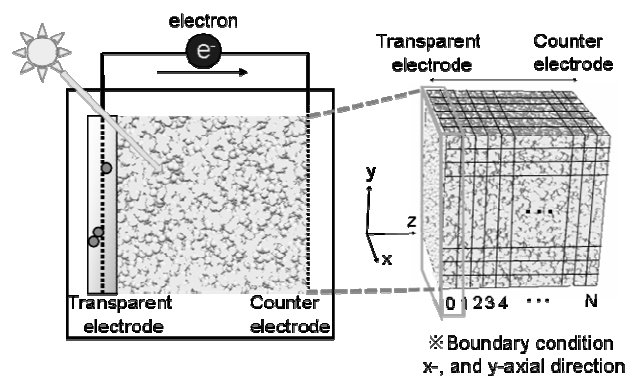


Fig. 2 Calculation model.

as shown in the previous study [2]. First, the calculation model was divided into voxels and the 0th to Nth cell along the z-axis as shown in Fig. 2 are defined. The initial placement of each electron within the TiO₂ particles is randomly determined. Electrons move in 6 directions in the three dimensional space with equal probability. We assumed that the electrons are trapped on the surface, and if an electron goes out of the TiO₂ particles, it is trapped within the trapping time, τ_r [4],

$$\tau_r = \frac{1}{N_C v_{th} \sigma} \exp\left(\frac{E_T}{k_B T}\right) \quad (1)$$

$$E_T = \frac{k_B T}{\beta} \ln(Rnd) \quad (2)$$

where N_C is the density of states in the conduction band, v_{th} is the electron thermal velocity, σ is the cross section of the trap, E_T is the energy of the trap, β is a measure of the width of the distribution, and Rnd is a random number between 0 and 1. After trapping, the electron is de-trapped and moves through within the TiO₂ particles. When an electron reaches the 0th cell, the transparent conductive electrode, it is

removed.

Current-Voltage Characteristic Simulation

Based on the results of the electron diffusion simulation, we estimated the current-voltage characteristics of DSSC devices. The total current density i is shown in Eq. (3),

$$i = i_1 + i_2 \quad (3)$$

$$i_1 = eD_e \frac{dn}{dz} \quad (4)$$

$$i_2 = e \frac{p}{\tau} (D_3 - 3D_1) \frac{dC_3}{dz} \quad (5)$$

$$\frac{di_1}{dz} = -e \int \Phi(\lambda) \alpha(\lambda) \exp(-\alpha z) d\lambda + e \frac{2nC_3}{2\tau_n C_3 + \tau_{co} n} \quad (6)$$

where i_1 and i_2 are the apparent current density within the TiO_2 porous structure and the electrolyte solution (I^-/I_3^-), respectively; e is the elementary electric charge; p is the porosity; τ is the tortuosity; D_e , D_1 , and D_2 are the effective diffusion coefficient of electron, I^- , and I_3^- , respectively ($\text{I}_3^- + 2e \rightleftharpoons 3\text{I}^-$); and C_3 is the ion concentration. The charge separation is shown in Eq. (6), which describes the essential behavior of DSSC. In addition, $\Phi(\lambda)$ is the intensity of incident light; $\alpha(\lambda)$ is the light absorption coefficient of sensitizing dyes; and τ_n and τ_{co} are the lifetime of electron and ion, respectively.

3. Results and Discussion

We constructed the calculation models by changing the porosity and the overlap ratio between TiO_2 particles. The average radius of TiO_2 particles was 10 nm. The cell size was $0.5 \times 0.5 \times 0.5 \mu\text{m}^3$. The calculation model was

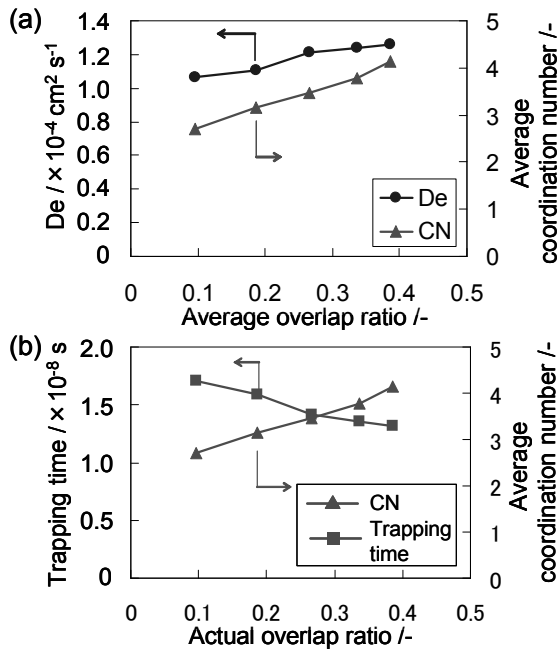


Fig. 3 Influences of the porosity and the overlap ratio on (a) D_e (●) and average coordination number (▲) and (b) trapping time (■) and average coordination number (▲) (for porosity 0.5).

divided into a $250 \times 250 \times 250$ mesh. We then performed the electron diffusion simulation under Δt of $4 \times 10^{-14} \text{ s}$ with a number of calculation step of 1.0×10^7 . The number of electrons was 12,500.

We simulated the influence on electron transport changing the overlap ratio between TiO_2 particles. The results are shown in Fig. 3. For a given porosity, the diffusion coefficient (D_e) increased with the increase in the coordination number of TiO_2 particles (Fig. 3(a)). On the other hand, the trapping time decreased (Fig. 3(b)). These results indicate that electrons can move more easily between n TiO_2 particles with the increase in the overlap ratio. The coordination number for the fixed porosity corresponds with the experimental results by Cass *et al.* [4]

We performed the simulation for the current-voltage characteristics of DSSC devices based on the results of the electron diffusion simulation. The results are shown in Fig. 4. For a given porosity, as the overlap ratio increased, the short-circuit current density (J_{sc}) decreased. This is because the specific surface area decreased and the generation of carriers decreased.

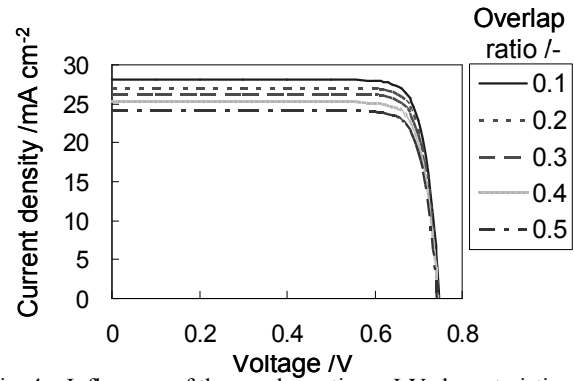


Fig. 4 Influences of the overlap ratio on I-V characteristics (for porosity 0.5, N3 dye).

4. Conclusions

In this study, we developed a multi-scale DSSC simulator. Our simulator successfully predicted the effect of overlap ratio between TiO_2 particles and the improvement of the electron diffusion properties of DSSC. Moreover, these results indicate that the simulator can quantitatively show the relationship between the porous structure and the performance characteristics of DSSC devices.

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