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Electron Diffusion Simulation of 3D Porous Structure for Dye-Sensitized Solar Cells

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1. Introduction

Since O'Regan and Grätzel reported a dye-sensitized solar cell (DSSC) in 1991 [1], it has been extensively studied because of its low-cost production with good energy conversion efficiency. However, the current maximum conversion efficiency is still about 11 %, and further efforts are necessary for higher conversion efficiency. For increasing the short-circuit current, which determine the conversion efficiency, it is necessary that TiO_2 porous structure have good properties of electron diffusion and all excited electrons are extracted at the transparent conductive electrode. The factors influencing the microstructure which affects the electron diffusion are porosity, the size of neck and so on. Because the experimental study is heuristic, it is important to obtain the insight from the computer simulation methods.

For predicting both material and overall properties of the system that are important to design a new electrode, we have developed the multiscale simulation approach for dye-sensitized TiO_2 porous electrode [2]. In this study, we developed a simulator for diffusion of electrons based on the three dimensional porous structure that realizes more accurate multiscale simulation environment. Using the developed simulator, we investigated the effect of a complex porous structure for the diffusion of electrons.

2. Methods

To construct the calculation models, we used the three-dimensional porous structure simulator "POCO[2]" [3]. This simulator can construct models of irregular porous structures based on an original overlap-allowed particle packing method. Figure 1 shows the calculation model.

Previous studies have showed that electron diffuses with repeated trapping and detrapping processes (multiple trapping) in the porous structure. Therefore we assumed same processes in the simulation. First, the calculation model was divided in a reticular pattern like in Figure 1. We defined the 0th cell and Nth cell along the z-axis as the transparent conductive electrode side and the counter electrode side, respectively. The two dimensional periodic boundary condition was applied to x- and y-axial directions. The initial placement of each electron is decided randomly within the TiO_2 particles. Electrons move in 6 directions of 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 TiO_2 particles, it is trapped between the trapping time τ_r s [4],

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

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

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 the trapping time, the electron detraps and moves through within the TiO_2 particles. When an electron reaches the 0th cell, the transparent conductive electrode, it is removed from the calculation system.

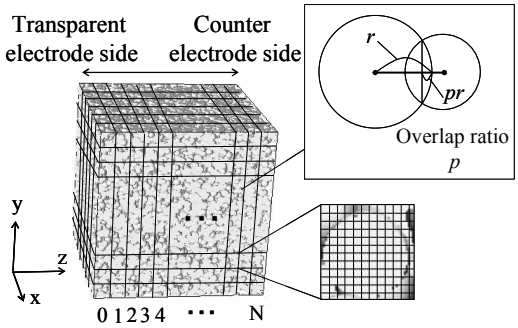

Fig. 1 Calculation model.

3. Results and discussion

We constructed the calculation models by changing the porosity and the overlap ratio p between TiO_2 particles. The average radius r of TiO_2 particles was 10 nm. The cell size was 0.5 × 0.5 × 0.5 μm. The calculation model was divided into 250 × 250 × 250 mesh. Then we performed the electron diffusion simulation under Δt of 4×10^{-14} s with a number of calculation step of 1.0×10^5.

Figure 2 shows the flux of electron that reached the transparent conductive electrode side and the average coordination number of the TiO_2 particles from each calculation model. From Figure 2(a), we found that the coordination number was increased with the increase of overlap ratio, on the other hand, the flux of electron that reached the transparent conductive electrode side changed little. In each porosity, it showed the same tendency. Also, from Figure 2(b), we found that the porosity and the flux of electron reaching the transparent electrode side were decreased with the increase of porosity. Therefore, the flux of electron reaching the transparent electrode is affected by the porosity rather than the coordination number.

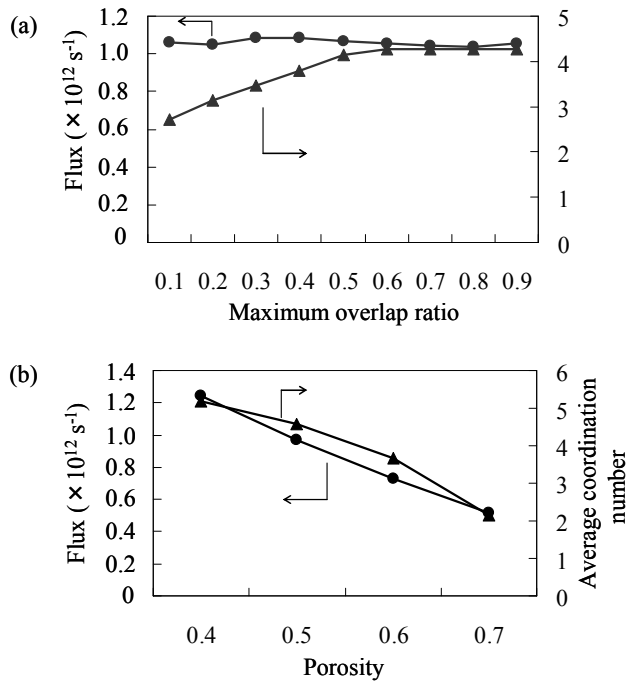

Fig. 2 The flux of electron that reached the transparent electrode side (●) and average coordination number (▲) for each model in case of (a) porosity 0.5 and (b) overlap ratio 0.5.

Next, we compared the summation of the trapping time from each model. Figure 3 shows the changes in trapping time and the coordination number with the overlap ratio (Figure 3(a)) and the porosity (Figure 3(b)). From Figure 3(a) it is seen that there is an increase in the trapping time with the decrease in overlap ratio. This tendency corresponded with the past study, which showed that the likelihood of electron encountering each trap is increased as the neck size decreases [4]. On the other hand, from Figure 3(b), as the porosity decreases, the coordination number was increased and the trapping time was decreased. Therefore, we showed that the electron trapping time is increased with the decrease of coordination number of TiO_2 particles. The increased trapping time caused the probability of recombination between electron and the oxidized dye or ion in the electrolyte to increase. Now we are trying to consider the effect of the dye and electrolyte on electron diffusion based on the quantum chemical calculation.

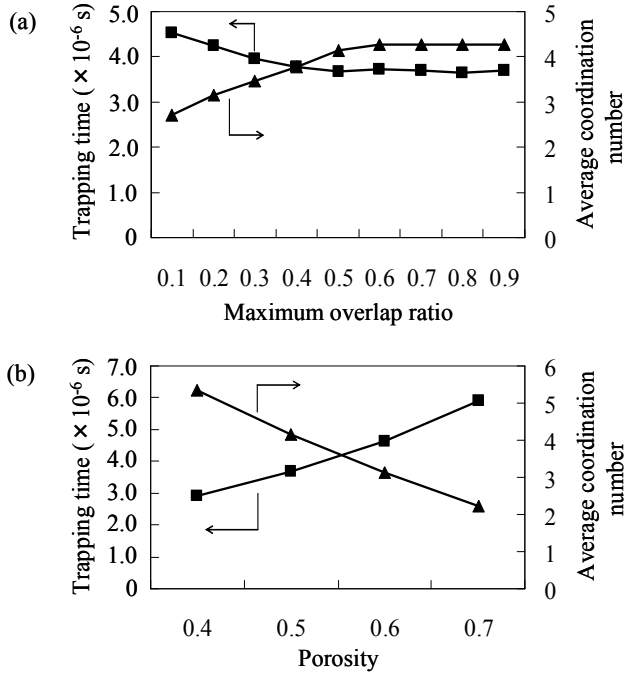

Fig. 3 Trapping time (■) and average coordination number (▲) for each model in case of (a) porosity 0.5, and (b) overlap ratio 0.5.

4. Conclusions

In this study, to investigate the effect of a complex porous structure to the diffusion of electron, we developed and applied the electron diffusion simulation using the calculation model with different porosity and overlap ratio constructed by the three dimensional porous structure simulator "POCO[2]". As a result, in case of same porosity, the flux of electron that reached the transparent conductive electrode is affected little by the coordination number of TiO_2 particles. On the other hand, the trapping time is increased with the decrease in coordination number.

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