

Does Network Geometry Influence the Electron Transport Dynamics in Mesoporous Nanoparticle Solar Cells?

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ABSTRACT

A major objective of our research is to define and solve the problems that limit the efficiency and commercial viability of solar cells based on dye-sensitized nanocrystalline TiO₂. Toward this end, we are currently elucidating the factors that govern charge transport and the loss mechanisms in mesoporous nanoparticle films of TiO₂. In this paper, we describe the first experimental evidence that the network geometry strongly influences electron transport and the first application of percolation theory to dye-sensitized solar cells.

1. Introduction

Dye-sensitized solar cells (DSSCs) are regarded as a viable economical alternative to inorganic photovoltaic cells owing to their moderately high efficiency (10.4% at AM 1.5) and potential low production costs. Despite their commercial promise, a number of important scientific issues that determine their performance are not well understood. One elusive issue is the elucidation of the principal factors that limit transport through the mesoporous films. Under normal solar intensities, the average time for the collection of photoinjected electrons in the nanoparticle films is in the millisecond-second domain, which is several orders of magnitude slower than the transport times for single-crystal TiO₂. We have shown that the slow collection time can be described quantitatively in terms of trap-limited transport [1]. Computer simulations, based on a random-walk approach and the assumption of an exponential distribution of trap depths, reproduce fully photocurrent transient data under the normal working conditions of DSSCs [1]. Until now, it has been assumed in the modeling of electron transport that network topology has no influence on it. Electrons are presumed to diffuse in three dimensions, restricted only by the macroscopic dimensions of the film and electrostatic interaction with the electrolyte (ambipolar diffusion [2]). In this paper, we discuss a recent study [3]. This study presents the first evidence that the network geometry strongly influences electron transport in mesoporous nanoparticle TiO₂ films and describes the first application of percolation theory to DSSCs [3].

2. Results and Discussion

Film characteristics. Figure 1 shows respective SEM images of 52%- and 71%-porous TiO₂ films composed of about 19-nm-diameter particles. A comparison of the two SEM images will show that the 71%-porous film has significantly more open space (dark areas) surrounding

the clusters of particles than the 52%-porous film. In both cases, the pores constitute more than half of the volume of the film. It can also be seen in Fig. 1 that there is no apparent long-range order in the nanostructured films [4].

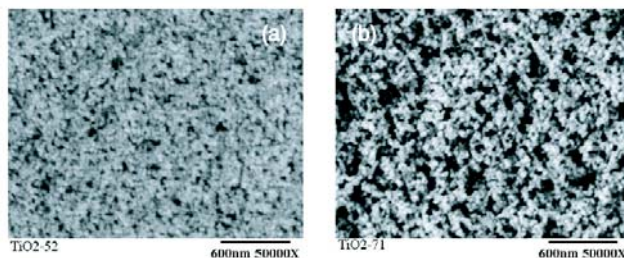


Figure 1. Plain-view SEM micrographs of (a) 52%- and (b) 71%-porous TiO₂ films.

Principal features of the physical structure of nanoparticle films can be described adequately by computer simulations [4]. Figure 2 shows the distribution of coordination numbers of the particles for film porosities ranging from 52% — 71%. At a film porosity of 58%, which is a typical film porosity used for the dye cell, about 10% of the particles have two neighbors, 25% of the particles have four neighbors, and less than 1% of the particles have eight neighbors. The average particle coordination number is 4.1. It can also be seen that as the porosity of the films increases from 52% - 71%, the distribution shifts from an emphasis on high coordination numbers to low ones. Furthermore, with increasing porosities, the fraction of single coordinated particles in a film increases dramatically. Such particles represent potential dead-ends in the electron transport pathways. An important implication of this discussion is that it is possible to manipulate the electron transport pathways through a nanoparticle network, making it more or less restrictive, by varying the film porosity.

Characterization of electron transport. The electron transport dynamics were characterized by transient photocurrent measurements. Figure 3 shows the dependence of the measured diffusion coefficient on the porosity of TiO₂ films for two electrolytes at a photocharge density of 10¹⁷ cm⁻³. It is seen that the cation used in conjunction with iodide in the starting electrolyte influences the magnitude of the electron diffusion coefficient. The rate of transport is larger in the presence of the tetrabutylammonium cation-based electrolyte than in the case of the 1-hexyl-2,3-dimethylimidazolium cation-based electrolyte, suggesting that the two cations interact differently with the TiO₂ surface. It is also seen that as the porosity increases, electron transport becomes slower. The

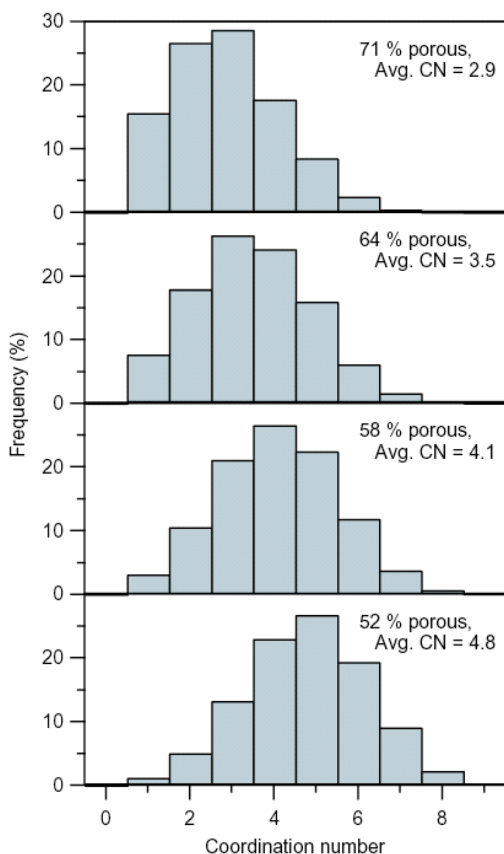


Figure 2. Dependence of the distribution of particle coordination numbers of simulated TiO_2 films on porosity.

solid lines correspond to the prediction of the percolation model — namely the electron diffusion coefficient displays a power-law dependence on the film porosity with respect to a critical porosity (i.e., a percolation threshold). The very good correlation of the percolation model to the experimental data indicates that the percolation model describes very well the effect of porosity on electron transport. The same values of the parameters (critical porosity and a power-law exponent), which were obtained from fitting the percolation model to the random-walk simulations of electron transport on computer-generated particle networks, also describe the experimental data. The theoretical curves are scaled only in the y-direction to fit the experimental data, corresponding to different prefactors for the two-redox electrolytes. From the perspective of the percolation model, the experimental observation is consistent with the notion that the TiO_2 film is made up of a random particle network and that the rate of electron transport through it is strongly influenced by the density of interconnected electron pathways, i.e., by the distribution of particle coordination numbers at a given porosity. The consequence of increasing the film porosity is to increase the tortuousness, and thus the length, of the electron transport pathway.

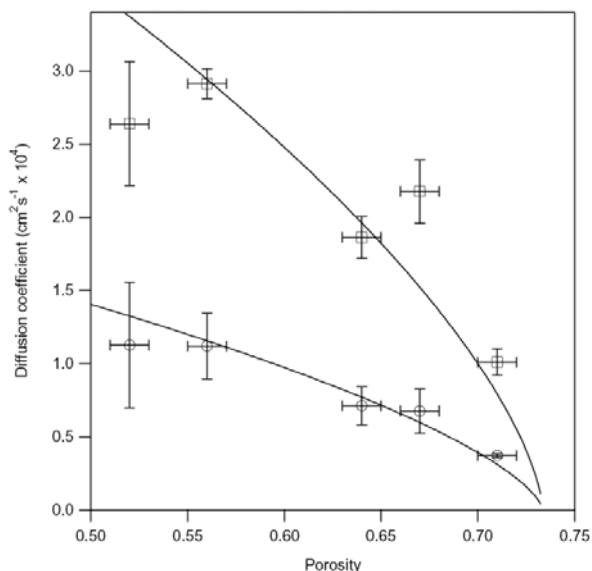


Figure 3. Dependence of the measured and predicted diffusion coefficient on the porosity at a photocharge density of 10^{17} cm^{-3} for two redox electrolytes in methoxypropionitrile: \square = 0.8 M tetrabutylammonium iodide and 0.05 M I_2 and \circ = 0.8 M 1-hexyl-2,3-dimethylimidazolium iodide and 0.05 M I_2 . Solid lines are fits of the percolation model.

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