Role of electron transfer dynamics in nano/sub-micro scale skeleton structured photoanode of dye sensitized solar cells

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ABSTRACT

Composed of sub-micron TiO_2 particles, the scattering layer covers the top of the optical active layer composed of nano TiO_2 particles to together form the "optical active layer/scattering layer", the double-layer skeleton microstructure of the photoanode in dye sensitized solar cells (DSCs). This type of photoanode extends the optical path of the incident light and enables repeated absorption of light, resulting in increase in the efficiency of DSCs. Since the optical active layer and scattering layer are integrally sintered and the materials have homogeneity, the study on influence of the scattering layer on the photoanode performance should not be limited to the optical properties. This paper investigates the non-optical properties of the scattering layer in detail, including electronic distribution, charge accumulation, transport/recombination dynamics, as well as the inherent influence of these properties on DSCs. The results show that the scattering layer can not only reflect light simply, but also has unique the electronic properties. Just like the optical active layer, the scattering layer can accommodate electrons. The electron transit time and lifetime in the scattering layer are faster than those in the optical active layer after the influence caused by the conduction band movement is removed. It is reasonable to infer that the main transport process occurs in the optical active layer and the recombination rate of the scattering layer is higher than that of the optical active layer within a certain bias range in a DSCs with the double-layer skeleton microstructure of the photoanode. So, the recombination process of electrons through the scattering layer may be a potential recombination path under the working conditions.

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1. Introduction

Solar power generation is an effective way to ease the energy crisis and has become the strategic choice for various countries in the world to realize their sustainable development. In order to develop an efficient photovoltaic conversion way, professor Grätzel from Swiss Federal Institute of Technology in Lausanne has invented a novel photovoltaic device, namely, dye sensitized solar cells (hereinafter referred to as DSCs), which create a new field for utilization of solar power generation [1]. As a multi-phase photoelectric chemical system essentially, a DSCs is a "sandwich" electrochemical cell, composed of conductive glass, dye sensitized

TiO_2 film, electrolyte and Pt counter electrode. DSCs have caused wide public concern about the unique structure design and rare photovoltaic conversion mode over the past few decades.

The photovoltaic conversion in DSCs includes important processes like that (1) Generation: The incident photons are absorbed by the dye molecules on the TiO_2 surface, and then the excited dye injects electrons into the conduction band of the TiO_2; (2) Transport: The photoelectrons are transported between the TiO_2 particles by diffusion toward the conductive substrate; and (3) Recombination: Some of the electrons in the TiO_2 film flow into the electrolyte solution, causing the energy loss. The aforementioned energy conversion processes occur in the core part, namely, photoanode, where the optical active layer is the nano-porous TiO_2 film with a relatively small particle size (about 20 nm). Such film has a high specific surface area and relatively poor light scattering performance [2]. The dye attached on the

TiO$_2$ surface determines the absorption range and intensity of DSCs. Each type of dye can only highly absorb the light within the specified band, so that the solar spectrum cannot be completely covered with a single type of dye. For example, the N719 dye has the highest absorption peak of about 530 nm, and most of the incident light at the band over 600 nm directly transmits though the sensitized film, rather than being absorbed, resulting in the light energy loss. In order to make full use of the light energy, an increased thickness of the optical active layer may improve the light absorption. Such method enables high increase in the optical path of the incident light and improves the light absorption of DSCs. However, thick optical active layer will bring a series of negative effects, i.e., if the electron diffusion length is less than the thickness of the optical active layer, the electrons cannot be collected [3]. Therefore, it is not advisable to increase the thickness of the optical active layer to extend the optical path of the incident light. The study showed that the performance of light scattering is greatly improved when the TiO$_2$ particles are developed into a sub-micron level [2,4]. The scattering layer composed of sub-micron TiO$_2$ particles covers the top of the optical active layer composed of nano TiO$_2$ particles and together form the "optical active layer/scattering layer", double-layer skeleton microstructure of photoanode. Such structural film enables the extension of the optical path of the incident light while being applied to the DSCs, the incident light can be absorbed repeatedly, and as a result, the efficiency of DSCs can be increased.

Many studies have been performed for electron injection, transport, recombination, collection and other processes of photoanode in DSCs. However, these studies all focused on the optical active layer. The researches on the scattering layer only highlighted on the optical properties such as absorption, reflection and transmittance. Because of the homogeneity of materials, the influence of the scattering layer on the performance of photoanode should not be limited to the optical properties in DSCs. This paper studied the non-optical properties of the scattering layer in detail, including electronic distribution, charge accumulation, transport/recombination dynamics, as well as inherent influence of these non-optical properties on DSCs.

2. Experiment & measurement

The agent including titanium isopropoxide for preparing TiO$_2$ paste, the agent including iodine (I$_2$), lithium iodide (LiI), benzimidazole (BI) and 3-methoxypropionitrole (MePN) for preparing electrolyte, and agent including 1-methylimidazole and iodopropane for synthesizing 1-methyl-3-propylimidazolium iodide, were all supplied by Fluka.

TiO$_2$ paste was printed on the transparent conductive glass (TEC-15, LOF) by use of screen-printing technology. A 11 μm thick nano-particle TiO$_2$ film (with a particle diameter of about 20 nm) was prepared on the TCO glass serving as the optical active layer and a 5 μm thick sub-micro TiO$_2$ film (with a particle diameter of about 300 to 400 nm) was prepared on another TCO glass serving as the scattering layer. Both films were sintered at 510 °C for 30 min in air and they have an area shown as 0.5 cm × 0.5 cm = 0.25 cm^2. The H$_2$PtCl$_6$ solution was sprayed on the transparent conductive glass, then sintered at 410 °C for 20 min to obtain Pt counter electrode. The gap between the film electrode and the Pt counter electrode was sealed with the thermal adhesive film (Surlyn, Dupont). The electrolyte solution, produced in that way that 0.08 M I$_2$, 0.6 M MPII, 0.1 M LiI, and 0.6 M BI were dissolved in MePN, was injected through the pore in the Pt counter electrode, and then the pore was sealed by a cover glass and thermal adhesive film, so that two kinds of electrochemical cells were

obtained, which were named the optical active layer and the scattering layer, respectively.

The electrochemical impedance spectroscopy (EIS) was measured at the electrochemical workstation (IM6ex, Zahner) in the dark. The modulation amplitude is 5 mV and the frequency ranges from 3 MHz to 80 mHz. The Zview software was utilized to fit the measured EIS so as to extract the impedance information.

3. Results and discussion

The electrochemical cell is a multi-phase system with a "sandwich" structure that mainly consists of conductive glass (TCO), TiO$_2$ film, electrolyte (EL), and platinum counter electrode (Pt-TCO). Two phases inside the electrochemical cell contact each other to form several interfaces: TCO/TiO$_2$, TCO/EL, TiO$_2$/EL and EL/Pt-TCO interfaces. The applied bias voltage can give rise to the electron transfer process at the contact surfaces [5]. In case of a positive bias, electron transfer takes place mainly at the TCO/EL interface because TiO$_2$ is in an insulating state. In case of a negative bias, the situation is more complicated. The TiO$_2$ film has the relatively low conductivity under a relatively low negative bias, and the electrons may be transferred at the TCO/EL interface and the narrow thin area close to TCO. In case of a relatively high negative bias, the TiO$_2$ conductivity is large, and the dominant electron transfer occurs at the TiO$_2$/EL interface due to a large surface area of the TiO$_2$ film. As one of the most important tools to study each interface process, EIS can show different interface impedance characteristics in case of external bias changes [6,7].

The TiO$_2$ material shows quite different electronic states, namely, the conduction band state, the exponential distribution state and the monoenergetic state [8,9]. Research showed that these electronic states play different roles in the photoelectric conversion of DSCs. In the conduction band state, the electrons can be quickly transported or directly recombined with the redox couples in the electrolyte solution. The exponential distribution of the band tail states in the bulk influences the electron transport and recombination of the conduction band through trapping/detrapping effect. The exponential distribution state and monoenergetic state on the particle surface can directly involve in recombination. The discussion above shows that the electronic states seem to exert a considerable influence over the transport and recombination. Fortunately, some of electronic states can be determined directly by measuring capacitance. Small changes of the Fermi level may cause the changes of the electron density under the corresponding state, so the parameter, chemical capacitance can be defined as follows [8,10,11].

For the conduction band state, the chemical capacitance C_μ^c can be shown as:

$$C_\mu^c = e^2 \frac{\partial n_c}{\partial E_F} = e^2 \frac{n_c}{k_B T} \tag{1}$$

where,

$$n_c = N_c \exp[(E_E - E_c)/k_B T] \tag{2}$$

For the exponential distribution of the band tail states in the bulk, the chemical capacitance C_μ^b is shown as:

$$C_\mu^b = e^2 \frac{\partial}{\partial E_F} \int_{E_v}^{E_c} g_b(E) f_b(E, E_F) dE \approx e^2 g_b(E_F) \tag{3}$$

where,

$$g_b(E) = \frac{N_b}{k_B T_b} \exp[(E - E_c)/k_B T_b] \tag{4}$$