Cracking deteriorates the efficiency in die-sensitized solar cells

Masato OHMUKAI[*], Akira TSUYOSHI[**]

ABSTRACT

We fabricated dye-sensitized solar cells with Ruthenium ion complex adsorbed in TiO_2 nano particles by mean of a low cost method and estimated their performance and the morphology of the active layer.　We achieved the best conversion efficiency with the solar cell having an active layer of 10 μm.　The fill factor increases with the film thickness till 30μm.　On the other hand, the conversion efficiency falls down when the thickness of the active layer becomes more than 10 μm. These samples showed many cracks in the active layers.　The cracks seem to leak the generated current in the solar cell.　Crack-free active layers are desirable for the realization of this kind of solar cells.

KEY WORDS: Ruthenium ion complex, color dye-sensitized solar cell, crack, fill factor

1．Introduction

Solar cells are now quite important devices for environment-friendly electrical power generation. Silicon-based materials are the most successful candidates in the practical use.　Compound semiconductor materials have been also studied for solar cells.　The biggest problem of these materials for solar cells is a high cost needed for the production.　On the other hand, dye-sensitized solar cells can be produced in a low-cost way without a sophisticated apparatus.　It is why dye-sensitized solar cells[1] attract much attention nowadays.　The energy conversion mechanism of this type is similar to the plant rather than pn junction of semiconductors.

The dye-sensitized solar cell consists of TiO_2 adsorbing Ruthenium ion complex (dye) and iodine electrolyte sandwiched by indium tin oxide (ITO) glasses.　The electronic dynamics in the cell has been widely studied[2-4]. The advantage of the cell is that the capture of light and electronic conduction is spatially separated.　Light is captured in the dye and electron flows in TiO_2.　Some researchers have done forming gels of the electrolyte[5-7], which is an important issue for the realization of products. On the other hand, various developments have been achieved in these days.　H. Nusbaumer et al. used Co ion complex as a dye[8], A. Kay et al. formed a complex film[9]. In addition, carbon nanotubes were applied to the cell.

The biggest problem of the dye-sensitized solar cell is the insufficient conversion efficiency.　The process technology of the cell should be developed to enhance the quality of the cell.　We then studied the effect of film thickness on the performance of the cell; such as conversion efficiency, fill factor and maximum generating electric power.　The amount of dye adsorbed in TiO_2 matrix is possibly critical for the conversion efficiency, and the problem is how to realize it.

2．Experimental details

We mixed 1 g of TiO_2 nanoparticles (the diameter was 30 nm) with acetyl-acetone (0.07 ml), polyoxyethylene-octylphenyl-ether (0.07 ml), and polyethyleneglycol (PEG) (0 ~ 150 mg).　As a solvent, water or diluted acetic acid (3 ml) was used.　These starting materials were put in a mortal and TiO_2 was well dispersed for 90 min.　The polyoxyethylene-

*電気情報工学科 **神戸高専

octylphenylether was used as a surface-active agent and the PEG was used to strengthen the viscosity of the paste.

The prepared paste was spread out on an ITO glass substrate by a bar-coat method and then annealed for 30 min. at 450 ℃ in a furnace. The thickness of the TiO_2 layers was determined with a micrometer by subtracting the thickness of the substrate. The substrate was soaked in a Ruthenium ion complex solution diluted with ethanol for 30 min. for the purpose of the adsorption of the dye to the TiO_2 layer. The substrate was put together with the other ITO glass coated with carbon. Finally, iodine penetrated in the interface.

The surface morphology of the TiO_2 layer was investigated with an optical microscope. Conversion efficiency was simply estimated with a fluorescent lamp as a light source. It is because our aim is not the determination of the absolute conversion efficiency under the sunlight. We ignored the difference of the efficiency caused by the spectral difference.

In this paper we describe 4 kinds of samples (A, B, C and D) with the thickness of 7, 10, 20 and 30 μm, respectively. When preparing samples A and B, acetic acid was used as a solvent. For the sample B, 50 mg of PEG was added where no PEG for the sample A. If more amount of PEG than 100mg was added, the viscosity of the paste was too high to form films. We then prepared samples C and D adding 100 and 150 mg of PEG, respectively with water as a solvent instead of acetic acid.

We measured I-V characteristics with a metal halide lamp (D250 by Toshiba Co. Ltd.) installed at a distance of about 60cm as a light source. The light from this lamp is characterized by the similarity to sunlight. The irradiance at the sample was 6.23 mW/cm^2.

3．Results and discussion

We show I-V characteristics of the solar cells of the samples A and B in the Fig. 1. The open voltage was 0.435 V. The shunted current density was around 0.55 mA/cm^2. The basic characteristics were similar to each other. The fill factors of the sample A and B were 0.34 and 0.35 respectively. On the other hand, the conversion efficiencies of the samples A and B were 1.3 and 1.4 %, respectively. From the two results, the sample B is a little bit better than the sample A. Further, as for the samples C and D, open voltage was 0.435 V regardless of the samples, where the shunted current was 0.19 and 0.15 mA/cm^2, respectively. We show the fill factors and efficiencies for all the four samples in Fig. 2 as a
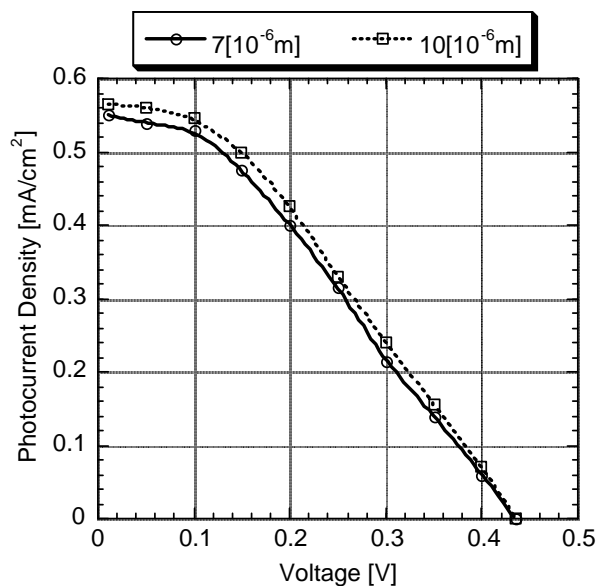

Fig. 1. The I-V characteristics of the samples A (t=7 μm) and B (t=10 μm).
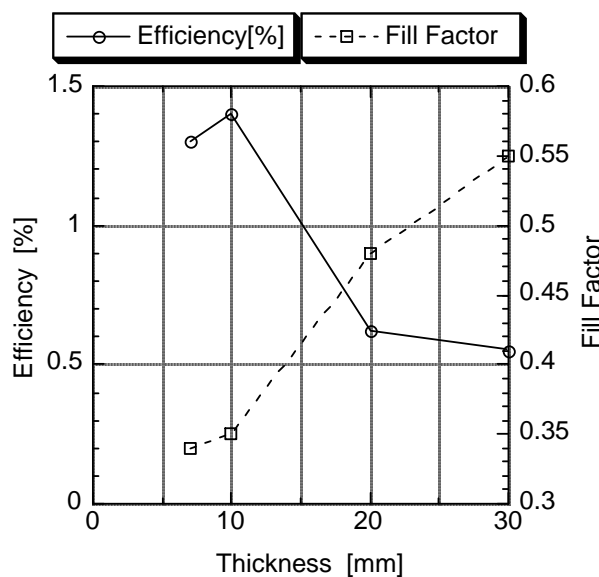

Fig. 2. The conversion efficiency and the fill factors as a function of thickness of the TiO_2 layer. The fill factor increases with the thickness, where the conversion efficiency fall down drastically over 20 μm. .

function of the film thickness. It is clear from the Fig. 2 that fill factor monotonically increases with the film thickness. On the other hand, the efficiency drops less than half when the thickness is over 10 μm. The maximum generating electric powers of the four samples (A-D) were 0.081, 0.088, 0.040 and 0.036 mW/cm^2, respectively.

It can be said that as the cell with the thicker active layer absorbs more light on condition that the thickness is under 10 μm; following the increase in efficiency with the thickness. When the thickness becomes more than 10μm, incoming light cannot reach the bottom of the active layer and the path for the electron in the active layer becomes longer at the same time. This suppresses the shunted current density as a result. The two contradictory conditions bring the maximum efficiency around the thickness of 10 μm.

We describe the surface morphology of the TiO_2 layers. Figures 3 and 4 are the photos of the sample B and C respectively using an optical microscope. The surface of the sample B is smooth without cracks (Fig. 3). But we found many small air bubbles all over the surface that were not so noticeable in the sample A. The air bubbles were included when the paste with TiO_2 was mixed in a mortal. From the fact that the sample B hold the better performance for a solar cell than the sample A, the existence of the air bubbles does not give a fatal effects on the electrical characteristics in a solar cell. This possibly lowers the durability of the cell.

Figure 4 shows many cracks over the surface. The sample D also showed the similar cracks as shown in Fig. 4. These samples C and D also included the air bubbles but not so much as the sample B. If the cracks exist, iodine electrolyte can directly reach ITO, which results in the leak of the generated current through the cracks. We therefore concluded that the cracks drastically deteriorated the efficiency of the solar cells. The cracks appeared possibly because the TiO_2 layer contracted at annealing. We could obtain the TiO_2 layers without cracks if the thickness was thin enough. However, the film thickness should be larger for a high fill factor. In order to avoid the cracks, careful forming process should be done such as annealing at low temperature for long-time or successive formation of thin TiO_2 layers.

4．Conclusion

We fabricated dye-sensitized solar cells by means of low-cost method. In our experiments Ruthenium ion complex was used as a dye and TiO_2 nano particle layer was spread with a bar coater. We achieved the conversion efficiency of 1.4 % with the solar cell of which the TiO_2 layer was as thick as 10 μm. When the thickness was 20 or 30 μm cracks appeared in the TiO_2 layer, which caused the conversion efficiency to fall down drastically in spite of the larger fill factors. It is suggested to be important to avoid cracks during the process. The air bubbles introduced in the
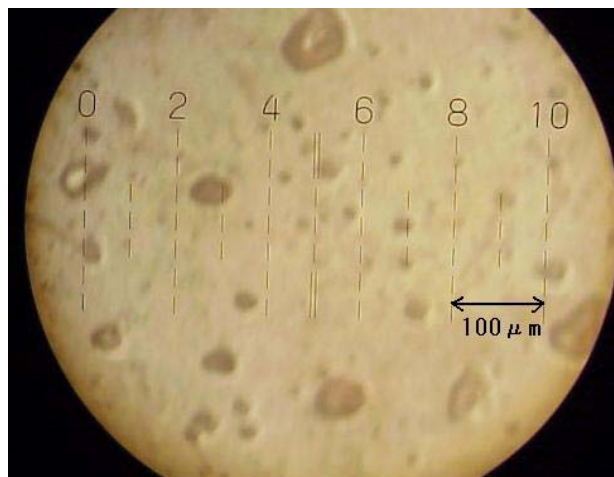

Fig. 3. The photo of the surface morphology of the sample B with an optical microscope. Many air bubbles are found.
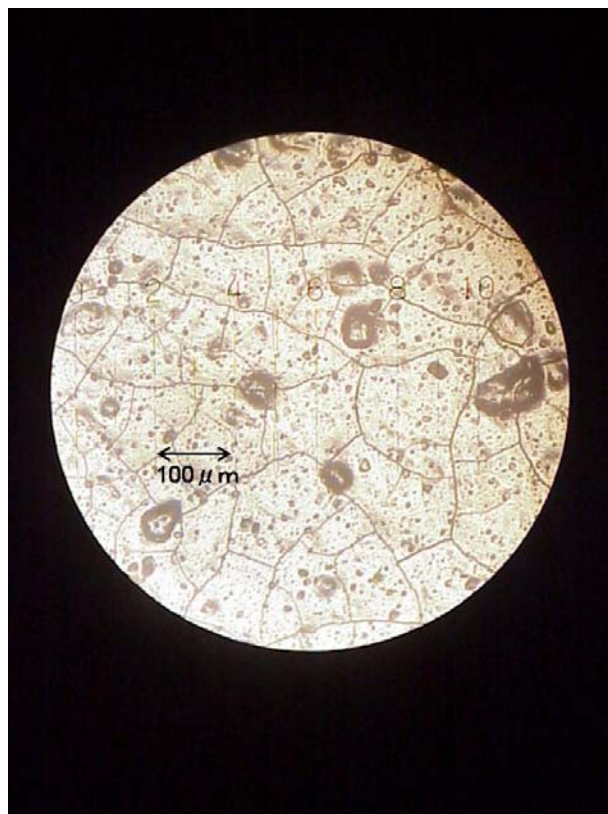

Fig. 4. The photo of the surface morphology of the sample C with an optical microscope. Many cracks are found on the surface.

TiO_2 layers on the other hand did not affect the performance of the solar cells so much.

References

1) W. Kubo, S. Kambe, S. Nakade, T. Kitamura, K. Hanabusa, Y. Wada and S. Yanagida: "Photocurrent-Determining Processes in Quasi-Solid-State Dye-Sensitized Solar Cells Using Ionic Gel Electrolytes", *J. Phys. Chem. B*: **107** (18) pp. 4374-4381 (2003).

2) R. J. Ellingson, J. B. Asbury, S. Ferrere, H. N. Ghosh, J. R. Sprague, T. Lian and A. J. Nozik: "Dynamics of Electron Injection in Nanocrystalline Titanium Dioxide Films Sensitized with [Ru(4,4'-dicarboxy-2,2'-bipyridine)$_2$(NCS)$_2$] by Infrared Transient Absorption", *J. Phys. Chem. B* **102** (34) pp. 6455-6458 (1998).

3) S. Kambe, S. Nakade, T. Kitamura, Y. Wada and S. Yanagida: "Influence of the Electrolytes on Electron Transport in Mesoporous TiO$_2$-Electrolyte Systems", *J. Phys, Chem. B* **106** (11) pp. 2967-2972 (2002).

4) R. Kawano and M. Watanabe: "Equilibrium potentials and charge transport of an I^-/I_3^- redox couple in an ionic liquid", *Chem. Commun.* (3) pp. 330-331 (2003).

5) P. Wang, S. M. Zakeeruddin, I. Exnar and M. Grätzel: "High efficiency dye-sensitized nanocrystalline solar cells based on ionic liquid polymer gel electrolyte", *Chem. Commun.* (24) pp.2972-2973 (2002).

6) W. Kubo, K. Murakoshi, T. Kitamura, S. Yoshida, M. Haruki, K. Hanabusa, H. Shirai, Y. Wada and S. Yanagida: "Quasi-Solid-State Dye-Sensitized TiO$_2$ Solar Cells: Effective Charge Transport in Mesoporous Space Filled with Gel Electrolytes Containing Iodide and Iodine", *J. Phys. Chem. B* **105** (51) pp. 12809-12815 (2001).

7) P. E. de Jongh and D. Vanmaekelbergh: "Trap-Limited Electronic Transport in Assemblies of Nanometer-Size TiO$_2$ Particles", *Phys. Rev. Lett.* **77** (16) pp. 3427- 3430 (1996).

8) H. Nusbaumer, Jacques-E. Moser, Shaik M. Zakeeruddin, Mohammad K. Nazeeruddin, and Michael Grätzel: "Co^{II}(dbbip)$_2$$^{2+}$ Complex Rivals Tri-iodide/ Iodide Redox Mediator in Dye-Sensitized Photovoltaic Cells", *J. Phys. Chem. B* **105** (43) pp. 10461-10464 (2001).

9) A. Kay and Michael Grätzel: "Dye-Sensitized Core-Shell Nanocrystals: Improved Efficiency of Mesoporous Tin Oxide Electrodes Coated with a Thin Layer of an Insulating Oxide", *Chem. Mater.* **14** pp. 2930-2935 (2002).