

Development of Dye-sensitized Solar Cells

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1. Introduction

Today, most solar cells manufactured in the world are silicon solar cells. There are several types of silicon solar cells, one of which is bulk silicon solar cells, which provide high conversion efficiency but require expensive materials. Then there are thin-film solar cells, which significantly reduce costs at the expense of decreased conversion efficiency. Non-silicon compound semiconductor solar cells are expected to provide conversion efficiency at the same level as silicon crystal solar cells, but raise concerns about environmental load and the use of rare metals. The "PV Roadmap 2030 (PV2030)" established by the New Energy and Industrial Technology Development Organization (NEDO) predicted that the accumulated amount of solar power generation introduced by 2030 would be about 100 GW (about 100 times the current amount produced), covering nearly half the electric power for household use (about 10% of total electric power). The Roadmap set a target for power generation costs at 7 yen/kWh. The power generation cost of current silicon crystal solar cells is about 40 yen/kWh and there is demand for the development of new low-cost high-efficiency non-silicon solar cells. One of next-generation solar cells

expected to satisfy these demands is dye-sensitized solar cells (hereinafter called DSC). Grätzel et al. reported high-efficiency cells using nanoporous titanium oxide semiconductor electrodes, ruthenium (Ru) metal complex dyes and iodine electrolyte solutions in the journal of Nature in 1991.¹⁾ Since then, many studies have been actively carried out on DSCs and revealed their performance comparable to amorphous silicon thin films.^{2, 3)} These DSCs have the advantages of low cost, lightweight and easy fabrication, but issues include durability and further improvement of their properties. To respond to these issues, many attempts have been made, such as solidifying electrolytes and improving materials and structures, but there have been no great breakthroughs yet.

This study was initiated with the aim of developing practical DSCs. This is a report on the consideration given to the optimum film thickness of the TiO_2 layer and the results of prototyping a hybrid cell.

2. Structure and Power Generation Mechanism of Dye-sensitized Solar Cells (DSC)

Figure 1 shows the structure and power generation principle of a DSC. It consists of a substrate with a trans-

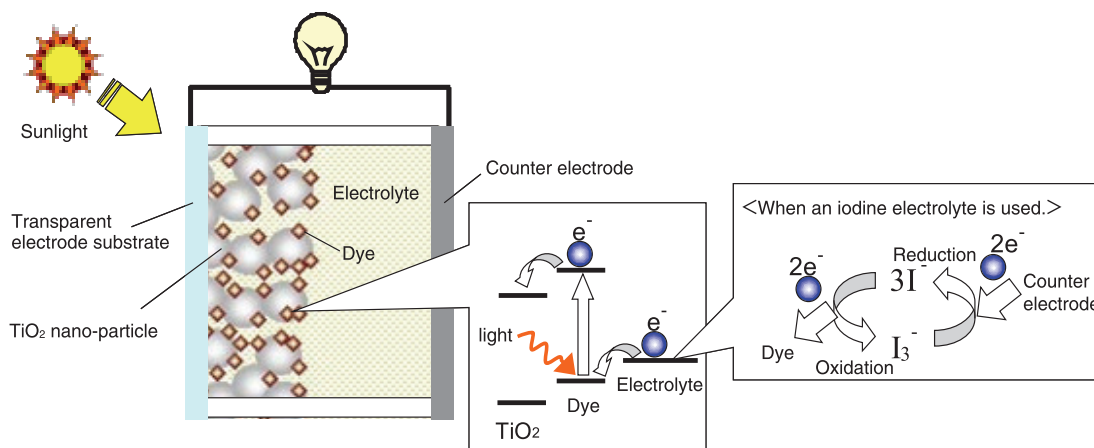


Figure 1 Structure and Power Generation Mechanism of a DSC

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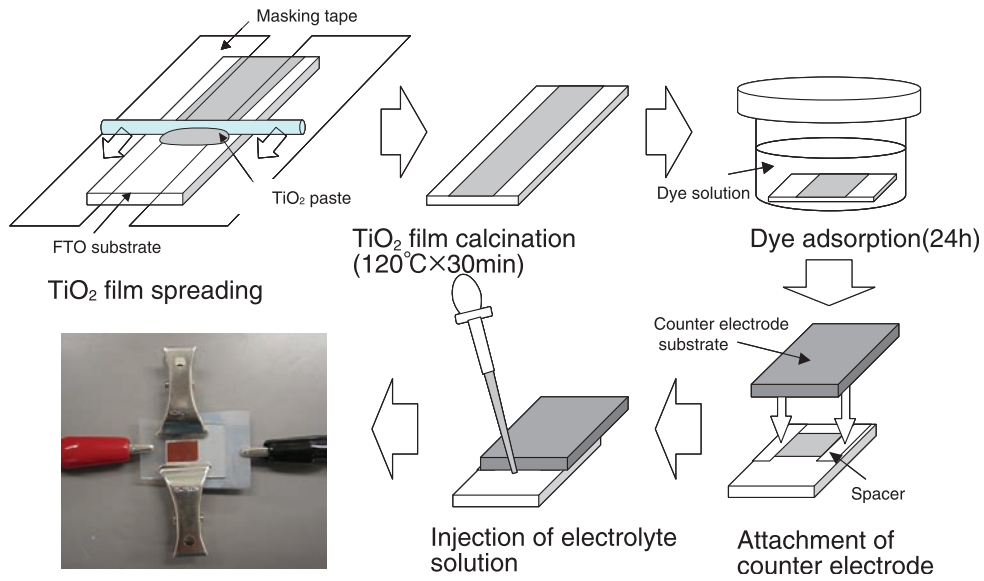


Figure 2 DSC Fabrication Flow

parent electrode, a dye adsorption titanium dioxide (TiO_2) nano-particle layer formed over it, an electrolyte, and a counter electrode substrate. In most cases, an electrolyte solution containing iodine redox couples is used as an electrolyte due to its performance. The power generation mechanism of a DSC structured in this way is described below. First, light is irradiated into a dye, exciting electrons in the dye. The electrons are injected into TiO_2 and diffuse, reaching the electrode. On the counter electrode, electrons are injected into the electrolyte and reduce I_3^- ions to I^- ions (when an iodine electrolyte is used). I^- ions diffuse in the solution, reach the dye, give up electrons, and are oxidized forming I_3^- ions. This cycle is repeated causing power generation by light irradiation.

The greatest feature of DSCs is the use of a TiO_2 nano-particle layer, which increases the specific surface area to about 1000 times the geometric area and thereby increases the dye adsorption area. In this way, electricity can be

easily extracted with a current density on the order of mA/cm^2 .

3. Fabrication of DSCs

Figure 2 shows cell fabrication processes. TiO_2 nano-particle paste (particle diameter of about 20 nm) is dropped on a fluorine-doped tin oxide (FTO) glass substrate masked with tape, and is spread with a glass rod to form a particle film. The thickness of the particle film is controlled by the number of applications. The paste applied substrate is calcined at 120°C for 40 minutes to bond particles and is then immersed in a solution of a Ru complex dye (N719 dye) in acetonitrile solvent at room temperature for 24 hours. After washing it, the glass substrate is attached to the counter electrode using spacers to make space for particles, and the iodine electrolyte is injected from edges.

Table 1 Film Thickness Dependence of Power Generation Properties

Number of applications of TiO_2	Film thickness (μm)	J_{sc} (mA/cm^2)	V_{oc} (V)	F.F.	η (%)
1	2.1	2.14	0.83	0.62	1.1
2	4.0	4.31	0.83	0.66	2.39
3	6.2	7.70	0.78	0.56	3.36
5	10.2	8.72	0.79	0.68	4.68
7	14.3	8.60	0.77	0.66	4.37
10	20.5	8.19	0.77	0.63	3.97

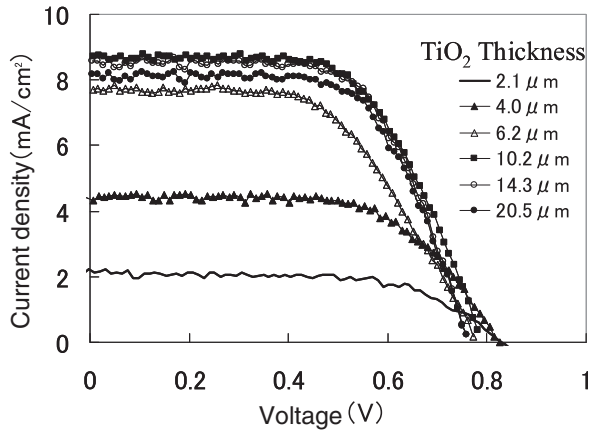


Figure 3 Film Thickness Dependence of I-V Characteristics

4. Verification of the Optimum Film Thickness of a TiO₂ Electrode Layer

The TiO₂ particle layer serves as an under layer for dye adsorption and a transport layer for electrons injected from the dye. It is known that its power generation properties greatly vary depending on changes in film thickness, particle diameter and other structural factors. In this study, we controlled the film thickness by varying the number of times the nano-particle paste was applied and evaluated the power generation properties. Repeated application was done by repeating the cycle of drying the applied paste at room temperature, applying more paste and spreading it on again. We used a surface roughness tester for film thickness evaluation, and we used a solar simulator (AM1.5, 100 mW/cm²) and a current-voltage (I-V) tester for measuring power generation properties.

Table 1 shows the TiO₂ film thickness dependence of I-V characteristics. Figure 3 is a graph of I-V curves. The current density linearly increased with the TiO₂ film thickness increase to about 10 μm, remains almost the same at

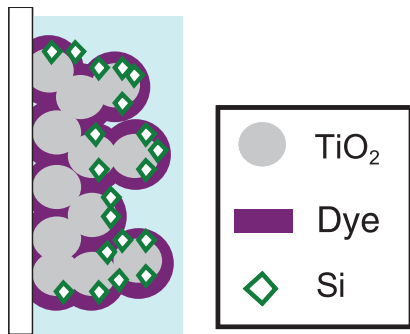


Figure 4 Schematic Diagram of a Hybrid Si/Dye Cell

TiO₂ film thicknesses within the range of about 10 μm to 14 μm, and slightly decreases at TiO₂ film thicknesses of about 20 μm. This behavior can be explained as follows. First, an increase in the TiO₂ film thickness increases the dye adsorption area. Therefore, the thicker the film becomes, the more electrons are injected from the dye into TiO₂. At the same time, as the film thickness continues to increase, electrons in TiO₂ need to move a longer distance to reach the transparent electrode. As a result, recombination occurs and carriers deactivate at a higher rate. The results of this verification indicate that there is less influence of carrier deactivation inside TiO₂ and the amount of current increases depending on the amount of dye adsorbed at a film thickness of about 10 μm or less. In the sample with a film thickness of about 14 μm, an increase in the amount of dye adsorbed and an increase in the rate of carrier deactivation counteract each other, and the amount of current ends up at almost the same level as that of the sample with a film thickness of about 10 μm. In the sample with a film thickness of about 20 μm, the influence of carrier deactivation becomes larger and reduces the amount of current compared to the 10 μm or 14 μm samples that adsorb less dye.

Recent reports have indicated that the optimum film thickness of a TiO₂ layer is around 10 μm,^{4, 5)} and, in this study, we obtained results consistent with those reports.

5. Hybrid Dye/Si-Sensitized Solar Cells

Ru complex dyes, predominantly used in the DSC field today, have an absorption wavelength range similar to that of a-Si, so they can absorb light mainly in the range of 400 to 700 nm which is good for exciting electrons. This

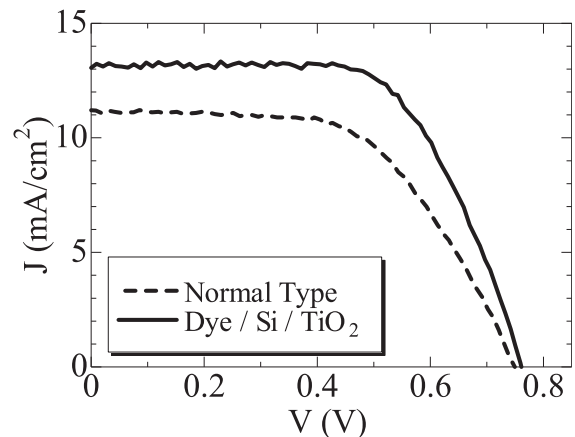


Figure 5 I-V Curves of a Conventional Cell and a Hybrid Cell

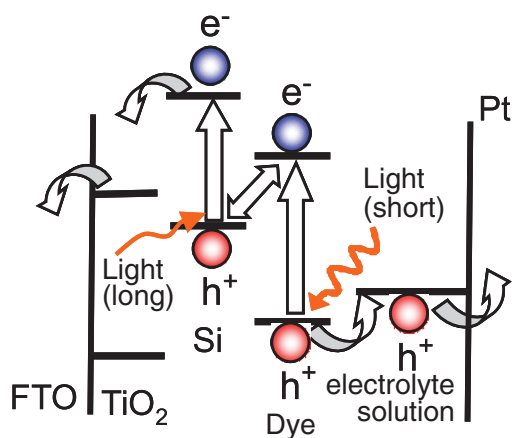


Figure 6 Power Generation Mechanism of a Hybrid Cell

means that this type of DSC ignores all near infrared and infrared rays at 800 nm or higher contained in sunlight. To solve this problem, long-wavelength dyes and tandem dyes with a wide range of power generation wavelengths have been actively developed⁶⁻⁸⁾, but they have not reached a practical level yet.

The performance of hybrid cells combining a Ru complex dye and a long-wavelength absorbing material are expected to improve over time. However, no satisfactory long-wavelength absorbing dye has been found yet. This study adopted silicon (Si), which has a narrow band gap that can absorb long wavelengths, aside from its practicality, for examination of performance of hybrid cells.

Figure 4 shows a schematic diagram of a hybrid dye/Si cell, in which Si particles are formed on a TiO₂ particle film using an arc plasma gun fabricated by the Advanced Electronics Equipment Division (refer to Reference 9 for details). A TiO₂ particle film with a thickness of about 10 μm was spread on a FTO glass substrate, and a Si layer was deposited from a Si target with 40 shots of sparks using an arc plasma gun. After that, the substrate was immersed in a Ru complex dye solution at room temperature for 24 hours for dye fixation. This substrate was attached to a counter electrode using spacers to make space for the particles, and an iodine electrolyte was injected from edges to make a cell. The power generation properties of the cell were measured with a solar simulator (AM1.5, 100 mW/cm^2) and an I-V tester.

Figure 5 shows I-V curves of the hybrid cell and a conventional cell. Hybridization has resulted in a substantial increase in current density and an improvement of conversion efficiency from 5.3% (for the conventional cell) to 6.5%. From this fact, we are lead to believe that the use of

Si allows long-wavelength rays to effectively contribute to power generation. We think specific factors are as follows. As shown in Figure 6, Si has a higher energy level than TiO₂ in a conduction band of an electron structure, so that electrons can be injected into TiO₂. On the other hand, the energy of holes in a Si valence band generated by electron excitation is lower than the HOMO level of the Ru complex dye and the redox levels of the iodine electrolyte solution. Therefore, the holes cannot be injected into directly. However, it is considered possible to generate a current by recombining these holes with excited electrons of the dye absorbing short-wavelength rays of sunlight, injecting the holes into the iodine electrolyte solution from the HOMO level of the dye, and flowing the carriers cyclically. When Si was fixed in the TiO₂ layer, the number of electrons injected from the dye to TiO₂ decreased, but more electrons were excited by absorbing long-wavelength rays of sunlight that cannot be absorbed by conventional cells, which resulted in the improved current density.

The results of this study indicate the effectiveness of the hybrid cell that combines a short-wavelength absorbing material and a long-wavelength absorbing material.

6. Conclusion

This study examined the optimum film thickness of a TiO₂ layer of DSCs and revealed that about 10 μm is the optimum thickness. A hybrid cell was prototyped by combining Si particles and a Ru complex dye, and it showed improved conversion efficiency at an increased current. Conversion efficiency of around 6% was easily obtained in this study, due to the simplified fabrication method, but conversion efficiency of 10 to 15% will be required for practical use. We aim to further improve the efficiency by introducing long-wavelength absorbing materials other than Si and developing sealing techniques.

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