

Highly Durable Dye-sensitized Solar Cells

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Dye-sensitized solar cell is expected to be one of the next-generation photovoltaics because of its low-cost and environment-friendly properties. Although we have developed some technologies and materials aiming to enhance its practical utility, the cell does not have sufficient reliability for out-door applications so far. The present study investigates newly developed robust solar cells with a novel protection layer of metal circuit and tightly sealed package. The resulting cells showed extremely high stability to pass several endurance tests standardized in JIS for stability of solar submodules, including an endurance test under the heat and humidity environment (85 °C, 85 % RH, 1000 h).

1. Introduction

The importance of the utilization of renewable energies such as photovoltaics has grown remarkably because of the escalation of fossil energy costs and demand for CO₂ reduction in order to prevent global warming. To fulfil these requirements, some new candidates of solar cells or photovoltaics have been invented and developed. Dye-sensitized solar cell (DSC)¹⁾, in particular, the one invented by Grätzel, is expected to be one of the next-generation photovoltaics because of its environment-friendly properties, low manufacturing cost and low manufacturing energy consumption. Recently, higher energy conversion efficiency was achieved on a small-sized DSC than practical amorphous-type solar cells²⁾. Now, the remaining problems of DSC for practical use are concerned with the unit cell size and structural design, fabrication process of cells and modules, and long-term stability under out-door operation. We have developed some technologies to solve these problems and applied them to our cells and modules that are low electric resistive electrodes with current-collecting grid³⁾⁴⁾ and leak-free nano-composite ionic gel electrolytes⁵⁾. However, in spite of the application of these technologies, DSC has not achieved sufficient quality so far, particularly, reliability for out-door applications.

Solar cells suitable for practical use are required to pass the JIS endurance tests, for example, JIS C 8938 “Environment and endurance test methods for amorphous solar cell modules” as shown in Table 1, and the recent aim of our research and development has been to achieve higher stability to pass the tests in this standard. Among these tests, the durability under light soaking was already reported⁶⁾⁷⁾, and it could be en-

Table 1. Excerpt of the test methods determined in JIS C 8938 “Environment and endurance test methods for amorphous solar cell modules”.

Thermal-cycling test	−40 °C ⇄ 90 °C 200 cycles
Humidity-freeze test	−40 °C ⇄ 85 °C / 85 %RH 10 cycles
Light soaking test	255 W/m ² (λ : 300 - 700 nm, spectrum : JIS D 0205) 500 h
Heat test	85 °C 1000 h
Damp heat test	85 °C / 85 %RH 1000 h

hanced with some modifications, such as UV-light protection. Thermal stability of DSC was reported only in small-sized cell, and most of the cells could keep their performance below 60 °C⁶⁾. There is no report concerning stability against high humidity to the best of our knowledge. Thus we considered it a higher priority issue to ensure resistance against the effect of humidity or high temperature.

2. Degradation factors of DSC performance

Figure 1 shows the fabrication process of a large-sized DSC⁴⁾. This DSC adopted current-collecting grid to expand photoactive area of the photo-anode since most of the fabrication process of the photo-anode can be built by simple screen-printing process. Counter electrode of this DSC was made of titanium metallic foil because it has mechanical flexibility for thermal expansion and makes the task of electric connection easy. Degradation factors of the performance of DSC are considered as follows: (1) leakage of electrolyte, (2) deterioration of electrolyte or electrodes and (3) corrosion of current-collecting grids. The risk of factor (1), however, is much lower than that in the conventional DSCs since our DSC uses a non-volatile, ionic liquid-based electrolyte instead of an organic solvent;

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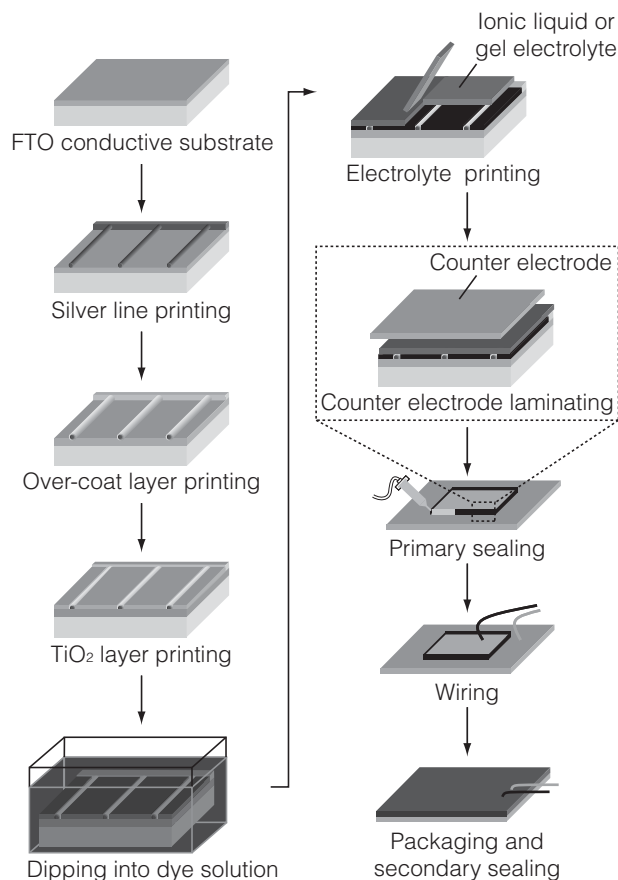


Fig. 1. Fabrication process of DSC using current-collecting grid and ionic liquid-electrolyte.

reduction in factors (2) and (3) were more important for achieving long-life stability.

2.1. Durability of electrolyte and electrodes

Although ionic liquid we employed does not itself freeze or volatilize in the temperature range between -40 and 90 °C, ionic liquid-based electrolyte contains typically volatile 4-*tert*-butylpyridine and iodine as additives⁵⁾ and has high hydrophilicity. Therefore, there are some risks of electrolyte deterioration by leakage of additives and intrusion of water from the outer atmosphere under high temperature and high humidity conditions. There are also concerns about degradation risk of electrolyte or electrodes at higher temperature. Leakage of the additives and time-course change of cell performance were measured by the following procedure to evaluate the degradation pathway under a high temperature test condition. A test cell, which has a photoactive area of photo-electrode of $50 \text{ mm} \times 10 \text{ mm}$ and a seal width of 2 mm , was prepared. Hotmelt resin and UV-curing resin were applied as the sealant of the cells. 10 pieces of the samples were encapsulated in a hermetically sealed container equipped with an irradiation window and sampling ports as shown in Fig. 2. After the samples were heated at 85 °C in the

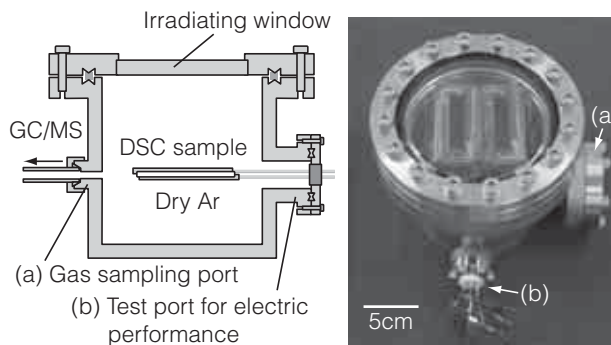


Fig. 2. Hermetic sealed container to measure leakage of electrolyte and photovoltaic performances.

Table 2. Amount of out-gasses of DSC in test container.

Sealant	Gas amount in test container (mg/L) ^{*1}		
	Iodine ^{*2}	TBP ^{*3,4}	Others ^{*4}
Hotmelt type	n.d.	n.d.	n.d.
UV-curing type	n.d.	0.001	n.d.

*1: Volume of container 0.61 L / Volume of electrolyte in DSC 0.185 mL

*2: Lower detection limit 0.002 mg/L

*3: 4-*tert*-butylpyridine

*4: Lower detection limit 0.001 mg/L

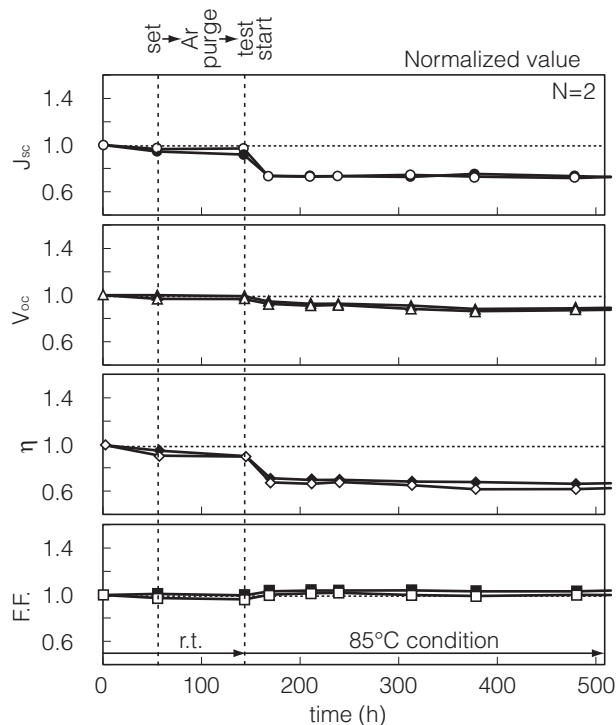


Fig. 3. Time course of the electric performance of DSC in the container.

container for 500 h , the leakage of the additives was measured by GC/MS analysis or detector tube method.

Table 2 shows the amounts of contents in the container after the test, and Figure 3 shows time-courses

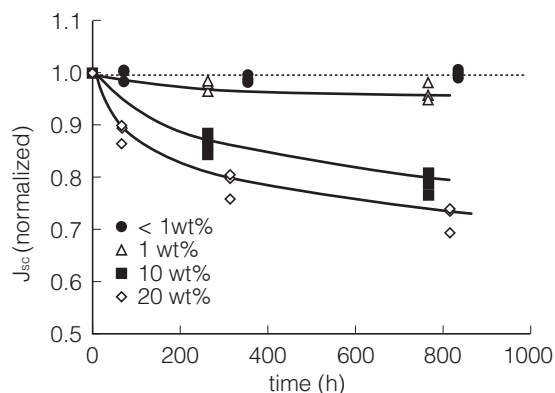


Fig. 4. Time course of J_{sc} of DSC with ionic liquid electrolyte containing different amounts of water.

of electric performance of the sample cells in the container. The amount of substances leaked out into the container from the cells sealed by hotmelt or UV-curing resin was very little, corresponding to the change in the composition of the cells which was less than 1 wt%. Electric performance of the cells became stable just after the start of the test, and it did not change much for a long time. Even though the performance change at the initial stage of the test was unclear, the thermal decomposition of electrolyte and electrode of ionic liquid-based DSCs was negligible.

It was anticipated that intrusion of substance like moisture from the atmosphere is more critical for degradation than the effect of heat. Decline of hole transfer by dissolution of platinum on counter electrode⁸⁾ and degradation of sensitizing dyes⁹⁾ were already pointed out as the negative effects of water in DSC electrolyte. Figure 4 shows time-courses of photovoltaic performance of DSCs containing water in the electrolyte. Drop of the short circuit current density (J_{sc}) of the cells was obviously enhanced as the water content in the electrolyte increased. Simultaneously, decolorization of red color of the photo electrode was accelerated. A similar color change was observed in long-term stored DSCs. These results suggest that the content or intrusion of water in the electrolyte must be less than 1 wt% to achieve long-life stability.

2.2 Durability of current-collecting grid

Current-collecting grid must be protected by a secure over-coat layer to avoid contact with I^-/I_3^- redox electrolyte since it would be reacted with and corroded by the electrolyte. Thus, the over-coat layer should be made with pinhole-less material such as low-melting glass, having an appropriate coefficient of thermal expansion; nevertheless, the over-coat layer would break on thermal stress and exhibit insufficient stability.

We found that the glass over-coat layer dissolved gradually into the electrolyte under high temperature

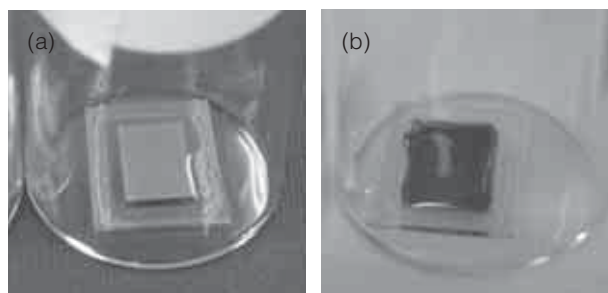


Fig. 5. Appearance of electrolyte solutions after contacting with over-coat layer for 1 month; (a) Electrolytes containing 10 wt% water kept under ambient atmosphere, (b) electrolyte without extra water kept in a dry box.

and high humidity conditions. Figure 5 shows low-melting glass samples dipped in an electrolyte containing 10 wt% of water and a dry electrolyte for one month. Although the dry sample did not change so much in its appearance, in the wet sample, the color of electrolyte originated from I_3^- ion was diminished by the reaction between water and the over-coat layer. The decolorized electrolyte lost hole conductivity completely, and it caused the performance of DSC to drop. Thus, it was found that moisture has considerable influence on long-life stability of current-collecting grid.

3. Durability improvement of DSC

3.1. Durability improvement of current-collecting grid

Hotmelt-type resin such as DuPont Surlyn is practically insoluble in electrolyte in contradistinction to low-melting glass and was reported as over-coat layer of current-collecting grid¹⁰⁾ in large-sized DSC. Although the resin over-coat layer could protect the grid from contact with the electrolyte hermetically at room-temperature, it could not do so sufficiently at 85 °C. Accordingly, we developed multi coated over layer using low-melting glass and resin to derive both the advantageous performances of sealing and protecting. The glass layer would seal the grid hermetically even at higher temperature, but some components would react and consume iodine and iodide in electrolyte. The resin layer cannot protect the grid by itself at higher temperature but has the property to protect the glass layer from reacting with the electrolyte. Figure 6 shows cyclic voltammograms of I^-/I_3^- redox couple, which illustrates change in the hole conductivity of cells in the presence of water in an electrolyte using the single glass over-coat layer or the double over-coat layer. While the color due to I_3^- ion has been diminished gradually in the case of the cell using single glass layer, the cell using double layer maintained sufficient redox ability even after soaking in 85 °C, indi-

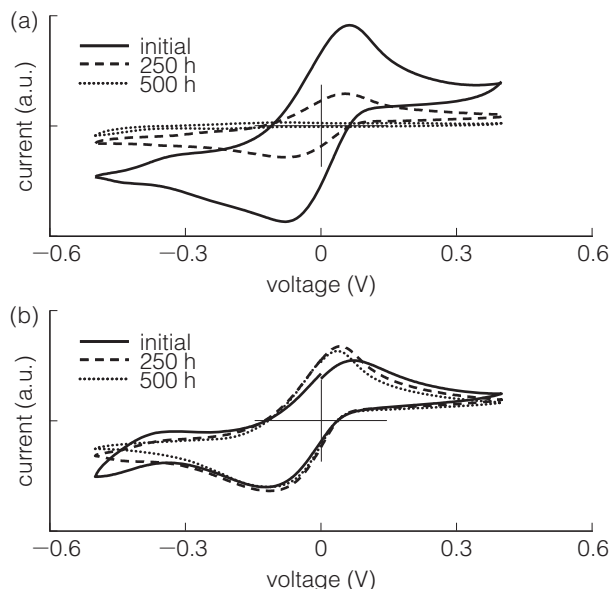


Fig. 6. Cyclic voltammograms of test cells using water containing I^-/I_3^- redox electrolyte and over-coat layer of current collecting grid; (a) conventional coating with low-melting glass, (b) novel coating with double layer.

cating that the second resin layer prevents the reaction between the first glass layer and the electrolyte.

3.2. Exclusion of moisture intrusion with packages

Additional higher gas barrier packaging was applied on DSCs to minimize the influence of moisture intrusion from the atmosphere. While our former DSC test cell used a resin to seal the electrolyte between working and counter electrodes and a plastic back-plate to protect back connectors¹¹⁾, novel DSC test cell was using three kinds of sealants in a single package as shown in Fig. 7. The first sealant, which hardly solved with the electrolyte, was used to avoid leakage of the electrolyte, and the second and third sealants using a resin and a gasket, respectively, was used to avoid moisture intrusion. Figure 8 shows time-course change of moisture intrusion into the cell under 85 °C and 85 %RH conditions. Quantity of moisture was indicated as relative humidity at room temperature measured by humidity test paper. Since some materials, such as water, plasticizers and so on, composing the package were vaporized at 85 °C, all the materials used in the package must be dried well before examination. The novel package kept its inner humidity lower than 10 %RH for at least 1000 h. The amount of water inside the package at a humidity of 10 %RH corresponds to a few ppm of water intrusion into the electrolyte in the cell, and it is much less than the original impurity of the ingredients. Thus, the influence of moisture intrusion into the cell was absolutely avoided using the novel package.

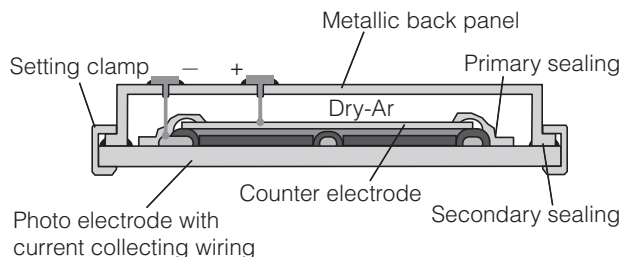


Fig. 7. A cross sectional structure of cell package.

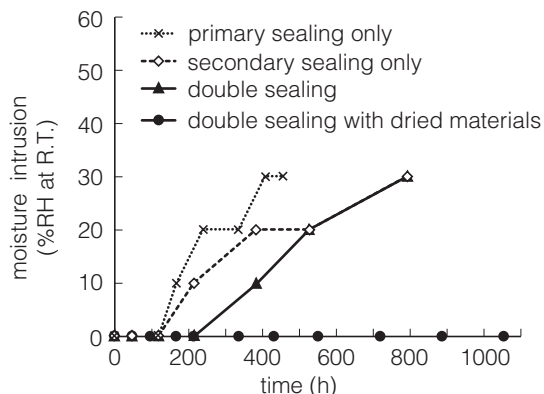


Fig. 8. Time course of water intrusion into the package under 85 °C / 85%RH conditions expressed in relative humidity at r.t.

4. Fabrication and test result

50 mm × 50 mm sized DSCs with ionic liquid-based electrolyte were fabricated using the double over-coat layer for current-collecting grid, and the novel package is shown in Fig. 9. Long-time stability tests according to JIS C 8938 were conducted. Figures 10 and 11 show results of the heat damp test and the heat cycling test, respectively. Although at the earlier stage within 300 to 400 h in heat damp test J_{sc} increased and the open circuit voltage (V_{oc}) decreased, the energy conversion efficiency (η) kept almost constant for the entire period. All indexes reached constant values thereafter, and properties of the cell had not changed so much for another 1000 h. Conversion efficiency after 1300 h dropped by 6 % from the initial value, but it was almost equal to that at 300 h. Result of the heat cycling test showed similar trend as increasing J_{sc} and decreasing V_{oc} in lesser degrees, and the performance changed by +10 % from the initial value after 200 cycles. Evaluation criteria of the heat cycling test and the heat damp test are described at JIS C 8991 “Thin-film terrestrial photovoltaic (PV) modules - Design qualification and type approval” and are -5 % from the initial stable value for both the tests. The DSC with the novel package had enough stability to pass the criteria. Figure 12 shows the result of a light-soaking test, where the DSC sample was soaked in simulated solar light for 500 h (1000 W/m², AM-1.5, surface temperature of the cell:



Fig. 9. An appearance of the robust DSC with novel package for the endurance tests.

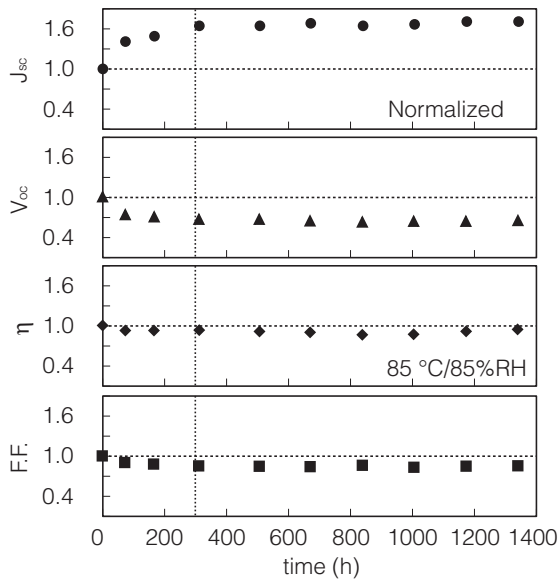


Fig. 10. Time course of electric parameters of DSC in novel package under the damp heat test.

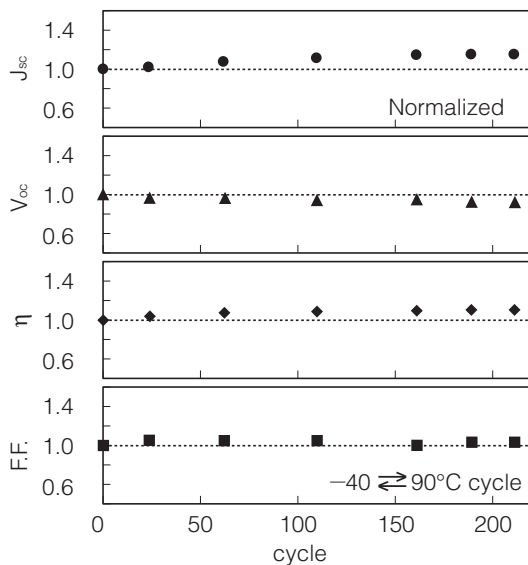


Fig. 11. Time course of electric parameters of DSC in novel package under the thermal cycling test.

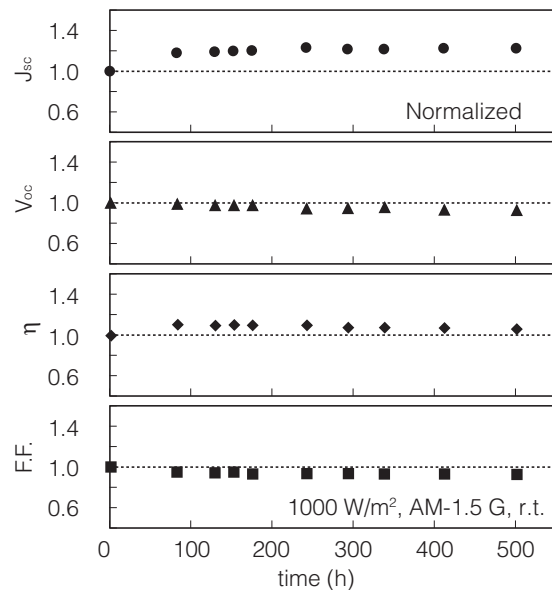


Fig. 12. Time course of electric parameters of DSC in novel package under the light-soaking test.

40 °C). This test condition is similar to the light-soaking test described in JIS C 8991, and the evaluation criteria of the test is within -10% from the initial stable value. Performance change of the DSC was -6% in this test, and DSC also had enough stability on the light-soaking test.

5. Conclusion

Novel DSC cells having improved heat, humidity and light-soaking durability were investigated. They successfully achieved sufficient durability to pass the JIS endurance tests by using a combination of the tightly shielded current-collecting grid and the humidity shutting out package. Before practically applying DSC, the relationship between the results of the JIS endurance tests and the actual long-life stability in practical out-door use must be evaluated. While the conversion efficiency of DSC module had not come up to that of conventional photovoltaics, the high durability obtained in this study was an important progress in the practical application of DSC. Further improvement to achieve a good balance between durability, energy conversion efficiency and tact time of fabrication process is an awaited task to overcome before commercialization.

Acknowledgement

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