Research Report

Long-term Stability and Degradation Analysis of Dye-sensitized Solar Cell for Outdoor Use

Naohiko Kato, Kazuo Higuchi, Hiromitsu Tanaka, Junji Nakajima, Toshiyuki Sano and Tatsuo Toyoda

Report received on July 11, 2011

Using the Raman spectroscopy in addition to the electrochemical impedance spectroscopy, we have clarified the deteriorated components of dye-sensitized solar cells module after the longest durability test in the world under the outdoor working condition for ~2.5 years. It was confirmed that the N719 dye adsorbed TiO₂ electrode and carbon counter electrode was almost stable, the photovoltages and the filling factors slightly decreased due to the increase of the Nernst diffusion impedance of triiodide (I₃⁻), resulting from the change of the components in the electrolyte based on γ-butyrolactone (GBL). Using the solvent-free ionic liquids electrolyte, the stability of the DSC was improved exceedingly, compared with the GBL electrolyte. The life time for outdoor use was estimated over 15 years from acceleration factor based on the outdoor exposure test. To confirm the stability of the DSC under practical outdoor use, we have fabricated the solar-powered night-light using the DSC modules, rechargeable batteries and bright light emitting diode (LED). The night-lights have been emitting a bright white light at night using the electricity from batteries charged by the DSC modules during the daytime in any weather condition at the outdoor sites close to the TOYOTA beam line of SPring-8 since May, 2009.

1. Introduction

Dye-sensitized solar cells (DSCs) have been expected to be a potential candidate of the next-generation solar cells having the advantage in costs and energy consumption for production, color choice and transparency. However, there has been only one report of the long-term outdoor stability of small size DSC, though there were a few reports about the visible light soaking test and the UV stability test of small size DSCs in the laboratory. Stability of practical large-size DSC modules have not been reported except for our previous report on a half year outdoor exposure test on the conventional parallel cell module, where the intrinsic lifetime of the DSC module could not be evaluated because of the leakage of the electrolyte after a half year which is attributable to poor sealing. In addition, the influence of series or parallel connection of cells on the long-term stability of the DSC modules was also not clear. To elucidate the intrinsic stability of the components of DSCs, we have fabricated the improved mini-modules (10 cm × 11 cm) including series-parallel connection of cells on a glass seat coated with transparent conductive oxide thin film (TCO glass), and conducted the long outdoor exposure tests (for more than 2 years) under working conditions. In the previous report, there was an absence of the direct evidence which components of DSCs have changed during long-term durability test. In this study, we have clarified the deterioration of the electrolyte based on γ-butyrolactone (GBL) solvent using Raman spectroscopy in addition to the electrochemical impedance spectroscopy. To improve the stability of the DSCs, we have also studied the stability of the unit cell using solvent-free ionic liquid electrolyte. We have also fabricated the solar-powered night-light using the DSC modules having solvent-free ionic liquid electrolyte, rechargeable batteries and a bright light emitting diode (LED) to confirm the stability of the DSC under practical outdoor use.

2. Experimental Section

2.1 Fabrication of Unit Cells, Modules and Solar-powered Night-lights

We have fabricated the mini unit cell as follows. The anatase TiO₂ electrodes were screen-printed on the TCO glass. The printed films after drying were
annealed at 450°C for 30 min in the air, which were followed by the surface treatment using TiCl₄ aqueous solution. The TiO₂ electrodes (the size of 10 mm × 7 mm) were dipped into a 3 × 10⁻⁴ mol/l solution of cis-di(thiocyanato)-(2,2'-bipyridyl-4,4'-dicarboxylic acid) (4,4'-dinonyl-2,2'-bipyridyl)-ruthenium(II) (Z907 dye) or a 3 × 10⁻⁴ mol/l solution of bis(tetrabutylammonium) [cis-di(thiocyanato)-bis(2,2'-bipyridyl-4-carboxylate-4'-carboxylic acid)-ruthenium (II)] (N719 dye) in 1:1 mixed solvent of acetonitrile and tert-butyl alcohol for one day to have dye molecules adsorbed to them sufficiently. A parallel cell was prepared using the dye-coated TiO₂ electrode as the photo-electrode and a platinum-coated TCO glass electrode as the counter electrode. The latter was prepared by chemical deposition of Pt from 0.05 M hexachloroplatinic acid at 400°C. The two electrodes were attached together using polyolefin-based sealant. The γ-butyrolactone solvent electrolyte (GBL-electrolyte) containing 1,2-dimethyl-3-propylimidazolium iodide, iodine, N-methylbenzimidazole, or solvent-free ionic liquids (imidazolium salts) electrolyte (IL-electrolyte) containing I⁻/I₃⁻ redox couple and the additives was injected into the cells.

We have fabricated the monolithic DSC modules as follows. On the one TCO glass (10 cm × 11 cm), nine stripe-shaped unit cells were fabricated. Adjacent three unit cells were monolithically interconnected in series to form three sets of series connected cells, which were connected in parallel using the silver collector electrodes. Each unit cell was fabricated by forming TiO₂ (anatase) photo-electrodes, TiO₂ (rutile) separators and carbon counter electrodes successively on a TCO glass, followed by a dye-adsorption process using N719 dye or Z907 dye. Each unit cell was separated from each others with polyolefin-based sealant. Finally, the backside was covered with a glass sheet having small pores for electrolyte introduction before outermost sealing was completed. The GBL-electrolyte or the IL-electrolyte was injected into each cell through the pores, and then the pores were sealed using polyolefin-based sealant. UV cut film was attached on the TCO glass sheet. A schematic cross section and a top view of the DSC module are shown in Fig. 1 and Fig. 2, respectively.

Finally, we have assembled the above-mentioned two types DSC modules employing Z907 dye and IL-electrolyte, the two rechargeable batteries (size AA batteries), and the white LED into a solar-powered night-lights. Two DSC modules were externally connected in series. The two batteries were also connected in series and generated a voltage of 2.4 V. The DSC modules, batteries and the LED were installed in the metal package having a transparent plastic window.

2.2 Evaluation of the Cells and Modules

The I-V characteristics of the unit cells and modules were determined by measuring photocurrent using an IV tester (IV-9701, WACOM) under the simulated solar insolation of AM1.5 G produced from a 1 kW xenon lamp and 400 W halogen lamp (WXS-155S-L2, WACOM), before/after the continuous 1sun light irradiation test at 60°C using xenon lamp in the laboratory. Impedance measurements of the unit cell before/after 3000 hours of the light soaking test were performed with a computer-controlled potentiostat (HZ-3000, HOKUTO DENKO) equipped with a frequency response analyzer (5080, NF ELECTRONIC INSTRUMENTS). The frequency range was 5 mHz-100 kHz. The magnitude of the alternative signal was 10 mV. All impedance measurements were carried out at open-circuit voltage under a bias illumination of
0.7 sun from a xenon light source. Raman spectra of each component of DSC module before/after the outdoor exposure test were obtained with JASCO NRS-3300 Raman spectrometer using the 532 nm laser. The several modules were set on the support horizontally and were protected with a waterproofed cover for outdoor performance test. The voltage of the module was kept constant at 1.6 V by the constant-voltage circuit during the solar insolation, giving the maximum output power (Pmax). The temperature of the module rose up to 72°C in summer daytime, and it went down to –10°C in winter night.

The several solar-powered night-lights were set up at outdoor sites close to the TOYOTA beam line of a synchrotron orbital radiation facility (SPring-8, Harima Science Park City, Hyogo, at latitude 35° north, Japan). The output voltage and current of the DSC modules were measured using data logger every 10 minutes under the outdoor working test. The short-circuit photocurrent (Jsc), the open-circuit photovoltage (Voc) of the modules were also measured occasionally by IV tester mentioned above.

3. Results and Discussion

3.1 The Long-term Outdoor Stability and Degradation Analysis of the DSC Module Using N719 Dye and GBL Electrolyte

Figures 3 show the changes of Jsc, Voc, the fill factor (FF) and the energy conversion efficiency (η) of the DSC module using N719 dye and GBL-electrolyte under the outdoor working condition. Each parameter was normalized using the initial value before the outdoor performance test. To our knowledge, this is the longest (for almost 2.5 years) stability test data of DSC module in the world under the outdoor working condition, though the slight degradation of the efficiency of the DSC module was observed (deterioration factor: \(-1.7 \times 10^{-4} / \text{day}\)). Since the leakage of the electrolyte was not observed, the observed degradation of DSC is attributed to the intrinsic one. The Jsc gradually increased with the outdoor exposure time (τ) until 0.4 years, and then became almost stable for about 2 years. The Voc and

![Fig. 3](image.png)

Fig. 3 Long-term stability of the DSC modules using N719 dye and GBL-electrolyte under outdoor working condition. The change of (a) Jsc, (b) Voc, (c) FF, and (d) efficiency of the DSC modules.
the FF gradually decreased with \( \tau \). The degradation of the efficiency was due to the decrease of \( V_{oc} \) and FF. The dark current measured by applying the voltage without irradiation of light also gradually increased with \( \tau \). The function of photoredox, that is, dye adsorbed TiO\(_2\) film, may be maintained, because the \( J_{sc} \) was almost stable except initial transitional period. The increase of the leak current from TiO\(_2\) to electrolyte may be expected from the decrease of \( V_{oc} \) and the increase of the dark current. Figures 4 show the changes of \( J_{sc} \), the \( V_{oc} \), the FF and \( \eta \) of the unit cell using N719 dye and GBL-electrolyte under a condition of continuous 1 sun light irradiation at 60\(^\circ\)C in the laboratory. The \( J_{sc} \) was almost stable, while the \( V_{oc} \) and FF gradually decreased with \( \tau \). The tendency of the change of the unit cell under continuous 1 sun light irradiation test was almost similar to that of the module under outdoor working test. Therefore, the series connection of small number of the unit cells had little influence on the long-term stability. The acceleration factor of the light irradiation test at 60\(^\circ\)C was estimated to be 11 by comparing the results in Fig. 4(d) with that in Fig. 3(d). This may give the indication of the specification of the stability test in the laboratory environment of the DSC modules.

Figure 5(a) shows the electrochemical impedance spectra as the Nyquist plots of the unit cell using N719 dye and GBL-electrolyte before/after the 1sun light irradiation test. The Nyquist plots had three semicircles. Each impedance component was assigned by Kern et al.,(13) Wang et al.(14) and Han et al.(15) The semicircle in the kHz range corresponds to the charge-transfer at the counter electrode, while the semicircle in the range of 1-100 Hz range is associated with the transport of photo-injected electrons in the mesoscopic TiO\(_2\) film and the back reaction at the TiO\(_2\)/electrolyte interface. The semicircle in the mHz range corresponds to Nernst diffusion impedance of triiodide (I\(_3\)) within the electrolyte. The semicircle in the mHz range became larger after the light irradiation test, indicating an increase of Nernst diffusion impedance of I\(_3\). Figures 6 show the Raman spectra taken from (a) the dye adsorbed TiO\(_2\) electrode, (b) the carbon counter electrode, and (c) the electrolyte in the DSC module using N719 dye and GBL-electrolyte before/after the outdoor exposure tests. The Raman spectra taken from the dye adsorbed TiO\(_2\) electrode showed that the N719 dye was almost stable, because the peaks of bipyridyl ligand and thiocyanato (NCS) ligand were maintained after the outdoor working tests. The vibrational assignments of dicarboxybipyridine group and NCS ligand are based on the previous reports.(16) The Raman spectra taken from the carbon counter electrode showed that the carbon was also stable, because the peaks attributed to graphite and the structural defects band have not changed. The assignments of the
graphite and the structural defects band here are based on the literature.\(^{17}\) It was confirmed that Jsc was almost stable during the outdoor working tests, because the structure of N719 dye adsorbed TiO\(_2\) electrode and carbon counter electrode was maintained. In contrast, the Raman spectra taken at the electrolyte changed after outdoor working test. The base line after the outdoor exposure test increased due to the emission of light, showing generation of the luminescent ingredients within the electrolyte during the outdoor working test. The existence of triiodide (I\(_3^-\)) could be detected at 115 and 226 cm\(^{-1}\).\(^{16}\) The concentration of I\(_3^-\) decreased after the outdoor working test. This fact corresponds to the increase of Nernst diffusion impedance of I\(_3^-\). The decrease of Voc and FF of the module after the outdoor working test was found to be due to the increase of the Nernst diffusion impedance of I\(_3^-\), resulting from the change of the ingredients of the electrolyte. This implies that the irreversible reaction between I\(_3^-\) and the contamination from outside, like water, possibly took place.

3.2 The improvement of the stability of DSC employing solvent-free ionic liquids electrolyte

Figure 7 shows the current-voltage curves under 1 sun irradiation of the cells having maximum \(\eta (\eta_{\text{max}})\) with N719 dye and GBL-electrolyte, N719 dye or Z907 dye and IL-electrolyte. The photocurrent was normalized by the Jsc of the cell with N719 dye and GBL-electrolyte. The \(\eta_{\text{max}}\) of N719 and IL-electrolyte was approximately increased by 110% compared to that of N719 and GBL-electrolyte, because the Jsc and the FF of N719 and IL-electrolyte increased by 120% and 106% compared to that of N719 and GBL-electrolyte, respectively, although the Voc of N719 and IL-electrolyte decreased by 86% compared to that of N719 and

**Figure 5** Electrochemical impedance spectra as the Nyquist plots of the unit cell before/after the 1 sun light irradiation tests at 60°C. (a) N719 dye and GBL-electrolyte, (b) N719 dye and IL-electrolyte, (c) Z907 dye and IL-electrolyte.

**Figure 6** Raman spectra taken from (a) the dye adsorbed TiO\(_2\) electrode, (b) the carbon counter electrode and (c) the electrolyte of the DSC module using N719 dye and GBL-electrolyte before/after the outdoor exposure test.
GBL-electrolyte. The $\eta$ of the cell with Z907 and IL-electrolyte was almost equal to that of the cell with N719 and IL-electrolyte. Figure 8 shows the changes of $\eta$ of the unit cells using N719 and GBL-electrolyte, N719 or Z907 and IL-electrolyte under a continuous 1 sun light irradiation at 60°C. The degradation rate of the cells with N719 or Z907 and IL-electrolyte was effectively suppressed, compared with N719 and GBL-electrolyte. Since the performance of the cell with Z907 and IL-electrolyte was similar to that of the cell with N719 and IL-electrolyte, we considered that the improvement of stability of the cell was mainly due to IL-electrolyte. To estimate the outdoor lifetime of the cell with ionic liquids electrolyte, we conducted the longer continuous 1 sun light irradiation test at 60°C over 15000 hours. Figures 9 show the changes of Jsc, Voc, FF and $\eta$ of the cells under this test. Each parameter was normalized using the initial value before the light irradiation test. The data of the cell with N719 and GBL-electrolyte was referenced as the cell of long-term outdoor exposure tests (for more than 2.5 years) in Fig. 4. Since the leakage of the electrolyte was not observed, we considered that the intrinsic degradation

![Diagram](image-url)

**Fig. 7** Current-voltage curves of the cells under 1 sun irradiation having maximum efficiency using N719 dye and GBL-electrolyte, N719 dye and IL-electrolyte and Z907 dye and IL-electrolyte. (Current was normalized by Jsc of the cell with N719 dye and GBL-electrolyte.)

![Diagram](image-url)

**Fig. 8** Changes of efficiency of the unit cells using N719 dye and GBL-electrolyte, N719 dye and IL-electrolyte and Z907 dye and IL-electrolyte under a continuous 1 sun light irradiation at 60°C.

![Diagram](image-url)

**Fig. 9** Long-term stability of the unit small cells under a longer continuous 1 sun light irradiation at 60°C. The change of (a) Jsc, (b) Voc, (c) FF, and (d) efficiency for the unit small cells using N719 dye and GBL-electrolyte, and Z907 dye and IL-electrolyte.
of DSC was observed. The retention time when \( \eta \) became 80% of the initial value was extended from 2800 hours of the cell with N719 and GBL-electrolyte to 15800 hours of the cell with Z907 and IL-electrolyte. The degradation of the efficiency of the cell with N719 and GBL-electrolyte was due to the decrease of Voc and FF. The Jsc of the cell with Z907 and IL-electrolyte gradually increased in the initial 2400 hours, after then gradually decreased, though the degradation rates of both cells were almost the same. Compared with N719 and GBL-electrolyte, the degradation rate of Voc of the cell with Z907 and IL-electrolyte was effectively suppressed. The FF of the cell with Z907 and IL-electrolyte was almost stable. The improvement of stabilized Voc and FF of this cell leads to the improvement of sustainability of \( \eta \). Table 1 shows the \( \eta_{\text{max}} \) and deterioration factor and the estimated outdoor lifetime. We defined outdoor lifetime in this table as the retention time when \( \eta \) became 90% of the initial value. The ratio of \( \eta_{\text{max}} \) of the cell using IL-electrolyte to GBL-electrolyte was 1.1. The cell with IL-electrolyte reduced the deterioration factor to one sixth of the cell with GBL-electrolyte. The outdoor lifetime of the cell with N719 or Z907 and IL-electrolyte was estimated to 15 years from the acceleration factor.

Figures 5(b) and (c) show the electrochemical impedance spectra as the Nyquist plots of the unit cell before/after the 1 sun light irradiation test. The semicircle in the mHz range of the cell with N719 and GBL-electrolyte became larger after the light irradiation test, indicating an increase of Nernst diffusion impedance of \( \text{I}_3^- \), resulting from the change of the ingredients of the electrolyte. The size of semicircle in the mHz range of the cell with N719 or Z907 and IL-electrolyte was almost maintained after the light irradiation test. This indicates that the cell using ionic liquids electrolyte reduce the change of the electrolyte. The more detailed analysis will be needed to clarify the deterioration mechanism of the cell using the ionic liquids electrolyte.

### 3.3 The Performance of the Solar-powered Night-lights Using DSC Module

The solar-powered night-lights have been emitting a bright white light at night using the electricity from batteries charged by the DSC modules during the daytime since May, 2009 as shown in Fig. 10. Figures 11 show the output voltage and current of the DSC modules during outdoor working test and Jsc and Voc of the DSC modules measured under the simulated solar insolation of AM1.5, 1 sun. The generated current was strongly affected by the weather, that is, it corresponded to the intensity of the solar insolation. The top value of the generated current was almost the same for a half year. In contrast, the voltage at the daytime in any weather was over 3 V and it did not change during the outdoor working test. Since the module voltage was higher than the voltage (2.4 V) of the batteries, the electricity could be charged in any weather. Therefore, the night-lights have been operating even if in the cloudy and rainy days. The Jsc gradually increased until initial 2 month and saturated after that. The Voc gradually decreased as the outdoor exposure time proceeds. The tendency in the change of Jsc and Voc of the modules corresponds to the results of the light soaking test of the unit cell. The performance of the DSC module will be maintained.

### Table 1

<table>
<thead>
<tr>
<th>Dye</th>
<th>Electrolyte</th>
<th>( \eta_{\text{max}} ) (Relative)</th>
<th>Deterioration factor (1/hour)</th>
<th>Outdoor Lifetime (year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N719</td>
<td>GBL</td>
<td>1.0</td>
<td>-7.8 ( \times 10^{-5} )</td>
<td>2.5 ( ^a ) )</td>
</tr>
<tr>
<td>N719</td>
<td>Ionic liquid</td>
<td>1.1</td>
<td>-1.3 ( \times 10^{-5} )</td>
<td>15.0 ( ^b ) )</td>
</tr>
<tr>
<td>Z907</td>
<td>Ionic liquid</td>
<td>1.1</td>
<td>-1.3 ( \times 10^{-5} )</td>
<td>15.0 ( ^b ) )</td>
</tr>
</tbody>
</table>

\(^a\) previous data\(^{(11)}\)
\(^b\) estimated value

---

© Toyota Central R&D Labs., Inc. 2011

http://www.tytlabs.co.jp/review/
over 15 years if there will be no trouble with sealing and the encapsulation of the module.

4. Conclusions

We have fabricated the monolithically series-interconnected DSC modules including parallel connection of cells on the one transparent conductive oxide (TCO) glass sheet. The longest intrinsic stability data of DSC module in the world under the outdoor working condition for almost 2.5 years was successfully obtained. The acceleration factor of the light irradiation test at 60°C was estimated to be 11 by comparing the deterioration factor of artificial light irradiation test and outdoor working test. The Raman spectroscopy and the electrochemical impedance spectroscopy revealed that the red dye adsorbed TiO₂ electrode and carbon counter electrode was almost stable, therefore the Jsc was maintained during the outdoor working. In contrast, Voc and FF decreased slightly as the outdoor exposure time proceeds, because the Nernst diffusion impedance of I₃⁻ increased, resulting from the change of the ingredients of the electrolyte.

Using the solvent-free IL-electrolyte, the stability of the DSC was improved exceedingly, compared with the GBL-electrolyte. The cell using IL-electrolyte reduced the deterioration factor to one sixth of the cell GBL-electrolyte. The life time for outdoor use was estimated over 15 years from acceleration factor based on the outdoor exposure test. Since the Nernst diffusion impedance of I₃⁻ of the cell using the IL-electrolyte after light irradiation test was maintained, it seemed that this cell reduced the change of the ingredients of the electrolyte.

We have assembled the solar-powered night-lights using the DSC modules, rechargeable batteries and bright LED to confirm the stability of the DSC under practical outdoor use. The DSC modules consisted of Z907 dye and IL-electrolyte. The night-lights have been emitting a bright white light at night using the electricity from batteries charged by the DSC modules during the daytime in any weather condition at the outdoor sites close to the TOYOTA beam line of SPring-8 since May, 2009.

Acknowledgement

We appreciate the cooperation of IMRA-EUROPE S. A. S. and AISIN COSMOS R&D Co., Ltd. in this work.

References


Junji Nakajima*
Research Field:
- Design of Solar Cell Modules
Award:
- Award of Tokai Chem. Ind. Assoc., 2006

Toshiyuki Sano*
Research Field:
- Process Design of Solar Cell Modules
Awards:
- Best Poster Award of Renewable Energy 2006
  - Award of Tokai Chem. Ind. Assoc., 2006

Tatsuo Toyoda*
Research Field:
- Solar Cell and Modules
Academic Societies:
- The Electrochemical Society of Japan
- The Japan Society of Mechanical Engineers
- Society of Automotive Engineers of Japan
- The Society of Iodine Science
Award:
- Best Poster Award of Renewable Energy 2006

*Aisin Seiki Co., Ltd.