



Research paper

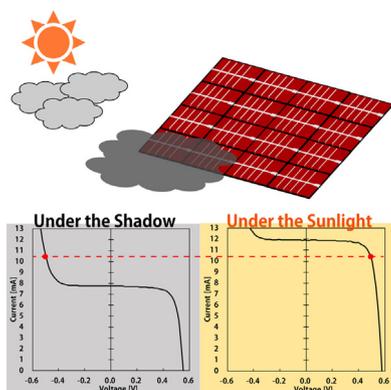
Stability of the current characteristics of dye-sensitized solar cells in the second quadrant of the current–voltage characteristics



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GRAPHICAL ABSTRACT



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ABSTRACT

Photovoltaic cells in series-connected modules may operate in the second quadrant of the current–voltage characteristics via power control circuits. In the second quadrant of the current–voltage characteristics of dye-sensitized solar cells (DSSCs), the forward currents continuously flow and the operating voltage points gradually shift toward more negative voltages. These changes are attributed to the increase in the ratio of iodide to tri-iodide in the DSSC electrolyte rather than to the decomposition and/or coupling reactions of the constituent materials. In addition, these changes are reversible reactions that can be detected based on the changes in electrolyte color or current–voltage measurements.

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1. Introduction

Dye-sensitized solar cells (DSSCs) are low-cost and low-energy organic photovoltaic devices with little environment impact (O'Regan and Grätzel, 1991). In addition, DSSCs can be added the characteristics of multi-colored and transparency to these surfaces

by several color dyes and transparent materials, and using thin-film materials as substrates allow flexibility (Otaka et al., 2004; Maetinez-Diaz et al., 2011). Enhancing the long-term stability of DSSCs is currently considered to be a technical challenge. We previously developed high-durability DSSCs using a sensitizer dye (Jiang et al., 2006; Noda et al., 2009; Imawaka et al., 2011, 2014). The DSSCs using this dye exhibited excellent stability. In particular, these energy conversion efficiencies maintained 95% or more from initial efficiencies after each of the four durability tests: a thermal aging test (+85 °C, 1000 h), a thermal cycling test (from –40 to +85 °C, 200 cycles), a continuous irradiation test (under standard

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air mass 1.5 (AM 1.5) solar spectrum light, 500 h), and an outdoor exposure test (over 300 days) (Noda et al., 2009; Imawaka et al., 2011, 2014). More recently, research institutions have reported DSSC results that approach the level required for practical application (Wang et al., 2003; Bai et al., 2008; Hara et al., 2009; Wu et al., 2010). Studies aimed to further improve the stability of DSSCs are in progress.

Practical techniques for the application of DSSCs are also being actively studied (Toyoda et al., 2004; Takeda et al., 2009; Hirsch et al., 2012). All photovoltaics, including DSSCs, must have a modular structure wherein several cells are connected in series for obtaining sufficiently high voltage for applications. However, the performances of the individual cells in the module are not always uniformly to be affected by shadows, clouds, and/or dirt when installed outdoors (Wheatley et al., 2001). In particular, the outputs of the cells in the modules of DSSCs are often non-uniform because of the market demands for multicolor and transparent cells. Fig. 1(a) shows three types of typical DSSC current–voltage (I – V) characteristics for the same size of photodetector but the different colors and transmittance of photodetector due to sensitizers and thickness of photodetector layers. Fig. 1(b) shows the I – V characteristics of a module comprising the cells shown in Fig. 1(a) connected in series. Fig. 1(a) indicates that the difference in DSSC components has a larger influence on short-circuit currents than on open-circuit voltages or fill factors. Fig. 1(b) shows that the I – V characteristics of series-connected cells with different short-circuit currents shape the step-like curve. When the module generates electrical power on the operating point A in Fig. 1(b), all individual cells are operated in the first quadrant via the power control circuit for photovoltaic generation. In contrast, when the module generates electrical power on the operating point B in Fig. 1(b), Cell-1 and Cell-2 are operated in the first quadrant, whereas Cell-3, which has the lowest short-circuit current, is operated in the second quadrant. In this case, a reverse voltage is applied to Cell-3 (as opposed to a forward voltage). When the reverse voltage reaches 1500 mV, the dye and electrolyte components of DSSCs have been reported to decompose (Wheatley et al., 2003). The current characteristics of DSSCs shown in the second quadrant of Fig. 1(a) are important in preventing the application of excessive reverse voltages to cells in series (Sastrawam et al., 2006; Okada and Matsui, 2012). Nevertheless, these current characteristics have not been well studied. This study aims to study the stability of the current characteristics of DSSCs in the second quadrant of the I – V characteristics.

2. Material and methods

Glass plates with antimony-doped tin oxide/indium tin oxide layers (GEOMATEC Co., Ltd.) were used as substrates for the cathodes and anodes of DSSCs. First, hexachloroplatinic(IV) acid paste (0.8 wt% as platinum) was printed on a substrate by screen printing and then sintered. Platinum metal was coated on the substrate by sintering. This substrate was utilized as the cathode.

Next, titanium oxide dispersion paste (PST-21NR, JGC Catalysts and Chemicals) was printed on a substrate by screen printing and then sintered. After sintering, the area of the porous titanium oxide layer was 100 mm² and the average thickness was 12 μm. By immersing the substrate into 120 mM titanium tetrachloride aqueous solution (Wako Pure Chemical Industries, Ltd.) for 30 min. and sintering again, the surfaces of the substrate and the porous titanium oxide layer were coated with fine particles of titanium oxide. In addition, the substrate was dipped in 0.3 mM SK-1 sensitizer solution for 120 min. (KNC Laboratories Co., Ltd.) (SK-1 in 1:1 acetonitrile:tert-butyl alcohol) to absorb the sensitizer on the surface of the titanium oxide layer. This substrate was utilized as the anode.

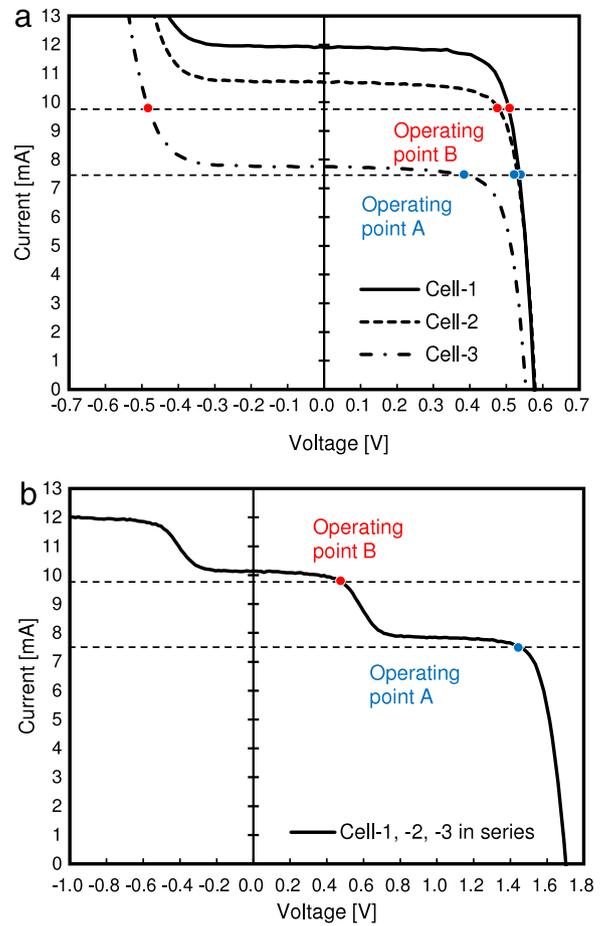


Fig. 1. Typical current–voltage (I – V) characteristics under standard air mass 1.5 (AM 1.5) solar spectrum light: (a) cells with different compositions and (b) a module comprising the serial connection of the cells shown in (a).

The titanium oxide coating strengthens the cohesion of titanium oxide particles and reduces serial resistance. Additionally, this coating prevents reverse electron transfer from transparent conductive layers to the electrolyte and is known to improve the electricity-generation characteristics in low-light conditions (e.g., indoors, cloudy weather, early morning, and evening).

The electrolyte comprised 0.1 M I₂, 0.8 M 1-methyl-3-propylimidazolium iodide (MPII), and 0.15 M 1-benzylimidazole (BEI) in 3-Methoxypropionitrile (3-MPN). DSSCs were fabricated by injecting an electrolyte between both electrodes and sealing the periphery with a UV-curing resin (UM, Nichiban).

The I – V characteristics were measured using a solar simulator (YSS-200A, Yamashita Denso Corporation), and reflection spectra were recorded using a visible light spectrophotometer (V-550, JASCO).

3. Results and discussion

First, a constant forward current was flowed from the anode to the cathode in the DSSCs by an external power source in the dark at 25 °C for 12 days and the I – V characteristics of the DSSCs were evaluated. Fig. 2(a) shows the I – V curves of the DSSCs that continued to receive a forward current of 3 mA/cm² for several days in the dark, and Fig. 2(b) shows the corresponding I – V curves under standard AM 1.5 global sunlight.

Fig. 2(a) shows that the threshold voltage of the forward current in the second quadrant in the dark is approximately –0.3 V. In

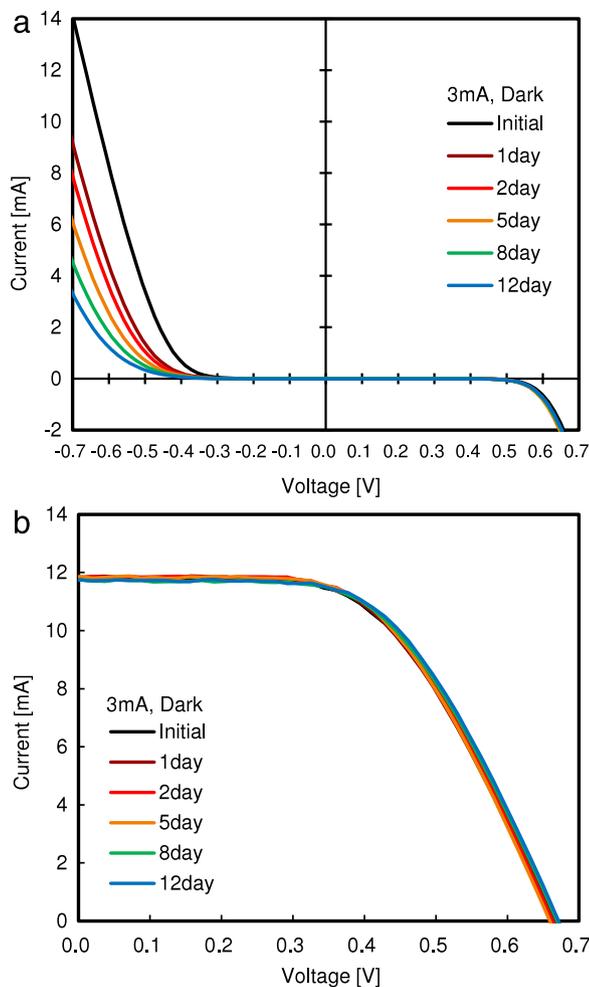


Fig. 2. I - V characteristics of dye-sensitized solar cells (DSSCs) through which a constant forward current of 3 mA/cm^2 has been flowed: (a) in the dark and (b) under standard AM 1.5 global sunlight.

addition, the current value of the I - V curve gradually decreases due to the flow of the forward current. In other words, the operating voltage points shift to more negative values. In contrast, in the first quadrant of the I - V curve under standard AM 1.5 global sunlight [Fig. 2(b)], no changes are observed in the open-circuit voltage, short-circuit current, and maximum output.

Next, a constant reverse voltage was applied to the DSSCs by an external power source in the dark at 25°C for 5 days and the I - V characteristics of the DSSCs were evaluated. Fig. 3 shows the I - V curves of the DSSCs to which constant reverse voltages ranging from 0 to -0.5 V were applied in the dark.

Fig. 3 shows that no significant changes were observed in the current characteristics at constant reverse voltages ranging from 0 to -0.3 V , which were less than the threshold voltage of the forward current in the second quadrant in the dark [Fig. 2(a)]. However, at constant reverse voltages ranging from -0.35 to -0.5 V , the current values of the I - V curve gradually decreased. In addition, the degree of reduction in the current value increased depending on the applied reverse voltage; that is, the current characteristics of the DSSCs in the second quadrant were affected by the forward current rather than the reverse voltage.

Because photovoltaic performance did not change under light irradiation, we considered that the observed changes in current characteristics shown in Figs. 2 and 3 were not due to variations in electron transitions from the redox level in the electrolyte to

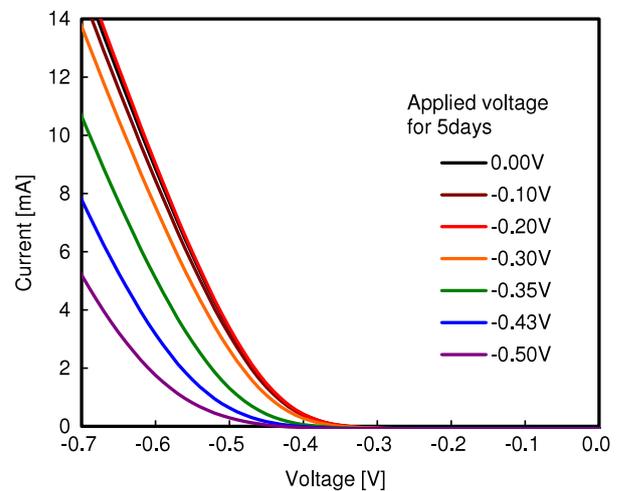


Fig. 3. I - V characteristics of DSSCs to which constant reverse voltages have been applied for 5 days in the dark.

the highest occupied molecular orbital of the organic dye or from the lowest unoccupied molecular orbital of the organic dye to the conduction band of the titanium oxide layer.

Thus, we focused on iodide (I^-) and tri-iodide (I_3^-), which are the main ions in the electrolyte (Asghar et al., 2012; Mastroianni et al., 2014; Asghar et al., 2016). Generally, the I^-/I_3^- ratio in the electrolyte of a DSSC is adjusted to achieve the highest photovoltaic performance under standard AM 1.5 global sunlight. During electricity generation in a DSSC, I^- is oxidized to I_3^- by the sensitizer in the anode, whereas I_3^- is reduced to I^- on the platinum catalyst. Therefore, the I^-/I_3^- ratio remains constant during electricity generation. However, when the forward current continues to flow in the DSSC, I^- is not sufficiently oxidized in the anode, causing the I^-/I_3^- ratio to increase and the current characteristics to change.

In the DSSC electrolyte, I^- and I_3^- show light-yellow and dark-yellow colors, respectively. To change the I^-/I_3^- ratio, a constant reverse voltage ranging from 0 to -0.5 V was applied to the DSSCs by an external power source in the dark at 25°C for 5 days and the reflection spectra of the electrolyte areas of the DSSCs were observed from the cathode side. From the acquired spectra, the intensities at wavelengths ranging from 510 to 650 nm (the yellow region from the DSSC electrolyte) were integrated. Fig. 4 shows the dependence of applied voltage values on the integrated reflection intensities of the electrolyte area.

Fig. 4 shows that the integrated intensities of the reflection spectra did not remarkably change from 0 V to approximately -0.3 V and gradually increases in less than approximately -0.3 V , depending on the decrease in the reverse voltage. This means that the color of electrolyte becomes pale depending on the reverse voltage, and this change is related to the increase in the I^-/I_3^- ratio. It was reported that the I^-/I_3^- ratio of the electrolyte also affects the first quadrant of the I - V curve under standard AM 1.5 global sunlight (Anderson et al., 2011). In this case, we think that this influence was not manifested yet, because the change of the I^-/I_3^- ratio by the reverse voltage was still small.

If these changes in the current characteristics are only temporary due to the compositional segregation of the electrolyte and are not caused by the decomposition and/or coupling reactions of the DSSC materials, these phenomena must be reversible.

The DSSCs to which a constant reverse voltage of -0.5 V had been applied in the dark at 25°C for 5 days were kept under various open-circuit environments, and their I - V characteristics were evaluated. Fig. 5 shows the I - V characteristics of these DSSCs after being kept under various conditions for 16 h.

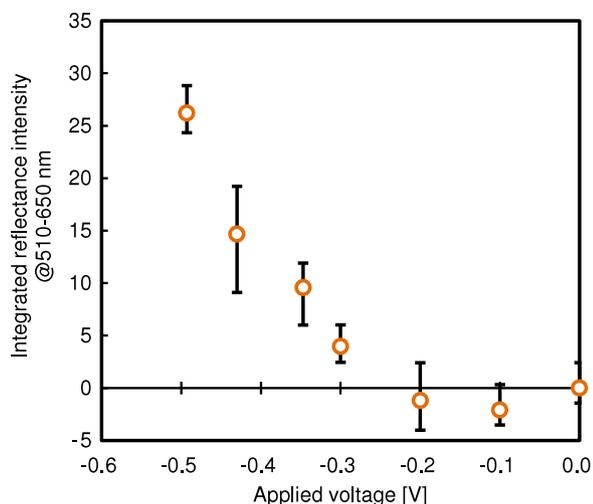


Fig. 4. The dependence of the applied voltage values on the integrated reflection intensities of DSSC electrolyte area.

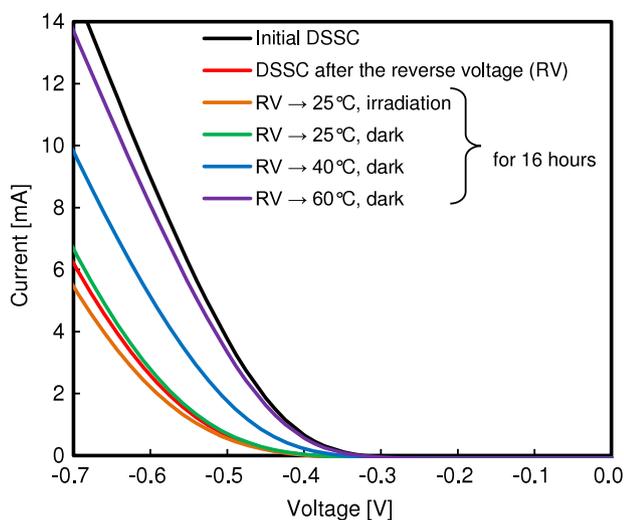


Fig. 5. I - V characteristics of DSSCs kept under various conditions for 16 h in the dark.

Fig. 5 shows that the characteristics of the DSSCs returned to their initial values when the DSSCs were maintained at 40 and 60 °C. In contrast, the characteristics did not recover within 16 h when the DSSCs were stored at 25 °C, regardless of the light irradiation environment. These results indicate that the value of the biased I^-/I_3^- ratio returns to its initial value by thermal annealing.

4. Conclusions

In this report, we evaluated the long-term stabilities of DSSCs operated in the second quadrant of the I - V characteristics in serially connected modules.

The threshold voltage of the forward current in the second quadrant in the dark is approximately -0.3 V. When this forward current continuously flows, the current characteristics gradually change and the operating voltage points shift to larger negative values. The results indicate that these changes are reversible reactions caused by an increase in the I^-/I_3^- ratio in the electrolyte rather than decomposition and/or coupling reactions of the DSSC materials.

For outdoor installations in summer or in warm regions, the DSSC module temperature can exceed 60 °C. Thus, we assume that segregation does not occur in the electrolyte due to unintentional thermal treatment. Further, it is difficult to identify the effect of thermal treatment in winter or in cold regions; therefore, the addition of new components, e.g., heating systems, is required. In addition, in indoor environments, where the intensity of light irradiation and temperature are stable, multicolor and/or transparency that cause extreme performance differences between individual cells should be avoided and changes in the electrolyte color should be considered.

It is difficult to identify changes in the performances of individual cells connected in modules. This report suggests that the reflection spectrum of the DSSC electrolyte may be a possible solution for detecting these changes.

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Conflict of interest

The authors declare no competing financial interest.

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