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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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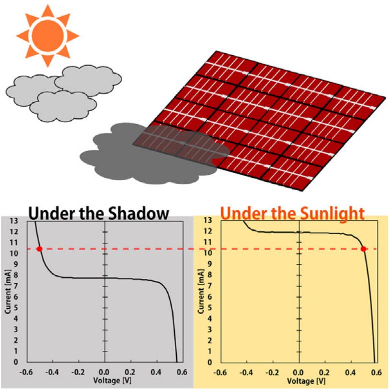
GRAPHICAL ABSTRACT



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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.

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; Hinsch 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 mm^2 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.

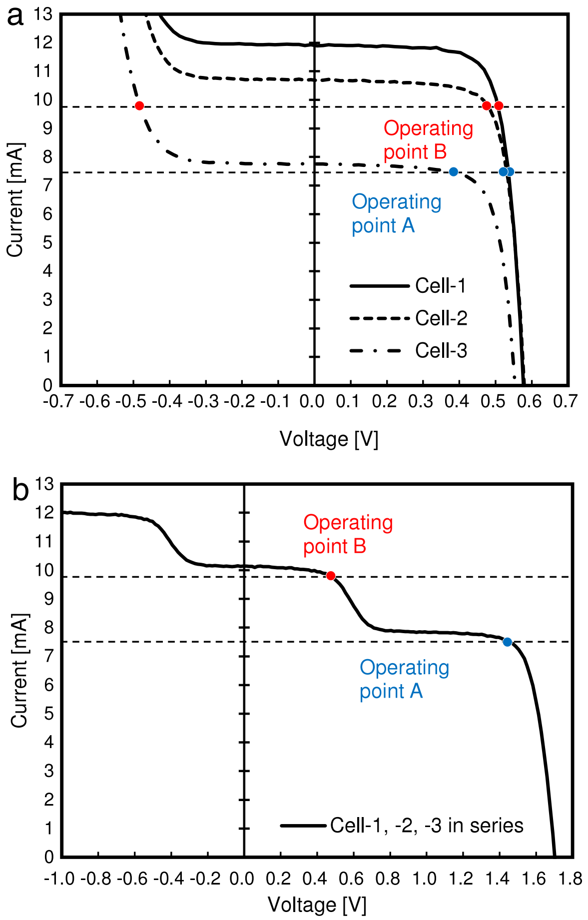

Fig. 1. Typical current–voltage (*I*–*V*) characteristics under standard air mass 1.5 (AM 1.5) solar spectrum light: (a) cells with different compositions and (b) a module comprising the serial connection of the cells shown in (a).

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 I_2, 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/cm^2 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