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Degradation analysis of dye-sensitized solar cell module consisting of 22 unit cells for thermal stability: Raman spectroscopy study

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Abstract

This study investigated the degradation of a DSSC module consisting of 22 unit cells for thermal stability. A 1000-h thermal stability test was conducted at 85 °C, after which the cells maintained ca. 73.5% of their initial overall power conversion efficiency (η). The degradation was also systematically investigated using Raman spectroscopy. The results revealed that loss of the overall power conversion efficiency was due to (i) desorption of the Z-907 dye from the TiO₂ electrode, and (ii) dissociation of SCN⁻ from the Z-907 dye. In addition, analyses of 2D Raman mapping determined the following factors after the thermal stability test: (i) the defect vacancy of Z-907 on the TiO₂ surface in the cell, (ii) the leakage of the desorbed Z-907 into the sealing material from the cell, and (iii) the dissociation of SCN⁻ ligand throughout the cell.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have recently received attention due to their economic competitiveness relative to conventional solar cells such as silicon-based photovoltaic devices (Wu et al., 2012). Because of the advantage of the DSSC, various approaches and studies have carried out, however, still many factors such as efficiency and stability of the system, sensitizer material, structure of metal oxide photoelectrode and electrolyte components remain to be optimized and improved (Hug et al., 2014). Among the fac-

tors to be improved, long-term stability is the most important key factor in commercialization. Although long-term stability of DSSCs has progressed gradually over the last 20 years, an achievement of long-term stability still remains a major challenge for commercialization of DSSCs (Hagfeldt et al., 2010; Hinsch et al., 2001). Z-907, an amphiphilic derivative of ruthenium dye, has been used as a substitute of N-719 because of its enhanced long-term stability, which is attributed to the hydrophobic moieties of Z-907 molecules (Zakeeruddin et al., 2002; Xia et al., 2007). In addition to the water-repelling property of its alkyl chains, they help prevent back electron transfer from the photoanode to the oxidized form of the sensitizer and the mediator by functioning as an effective insulating barrier (Schmidt-Mende et al., 2005). Z-907 based DSSC was already shown to have remarkable long-term stability at 55 °C after

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light-soaking for 1000 h, and to maintain 94% of its initial conversion efficiency after exposure for 1000 h at 80 °C (Wang et al., 2003). Therefore, Z-907 based DSSC is considered a practical device for outdoor application. However, the DSSC modules that show outstanding light-to-electric power conversion and long-term stability are less than or equal to 1 cm², and efficiency decreases as size increases (Lenzmann and Kroon, 2007; Matsui et al., 2009). Unfortunately, long-term stability of large-area modules has yet to be resolved, in addition, durability under heat stress is necessary, which is directly related to outdoor performance.

In the present study, a DSSC module $(30 \times 30 \text{ cm}^2)$ consisting of 22 stripe-shaped unit cells was used to evaluate the long-term stability of this DSSC module. This module was exposed at 85 °C for 1000 h and the degradation of DSSC was analyzed via Raman spectroscopy. Several studies have reported Raman spectroscopic analyses of the degradation of DSSC modules at the unit cell level, but not the module level. Moreover, analyses of the longterm stability via Raman spectroscopy were carried out after decomposition of modules (Xue et al., 2012; Kato et al., 2009). Raman spectroscopy is a powerful and facile analytical tool because it enables qualitative analysis without any pretreatment of samples. Therefore, to fully utilize the characteristics of Raman spectroscopy as a nondestructive analytic method, both Raman scattering measurement at one point and 2D Raman mapping in a large area were conducted to analyze the degradation of DSSC to determine long-term stability. 2D Raman mapping is a useful technique for analysis of the existence and distribution of composites in a large area. Thus, 2D Raman mapping was utilized to investigate the degradation of DSSC module by distinguishing the adsorbed condition of the dye on the photoelectrode and changes in molecular structure during area analysis of the DSSC module (Bräutigam et al., 2012; Liu et al., 2014).

2. Materials and methods

2.1. Fabrication of DSSC modules

A DSSC module $(30 \times 30 \text{ cm}^2)$ consisting of 22 stripeshaped unit cells was obtained from Eagon Windows & Doors Co., Ltd. The total active area of the module was 0.05 m². Fig. 1 shows the schematic diagram and the actual photo image of the DSSC module fabricated on a TCO glass. Briefly, the unit cells were monolithically interconnected in series to form one module. Each unit cell was fabricated first by forming TiO₂ photoelectrodes on TCO glass, followed by dye-adsorption using cis-bis(isothiocyanato)(2 ,2'-bipyridyl-4,4'-dicarboxylato)(4,4'-di-nonyl-2'-bipyridyl) ruthenium(II) (Z-907) (Dyesol, Australia). The backside, which contained the Pt counter electrode formed by electrodeposition, contained tiny pores for introduction of the electrolyte, which consisted of 3-methoxypropionitrile (3-MPN), 1,2-dimethyl-3-propylimidazolium iodide (DMPII), and iodine. The pores were sealed using a polyolefin-based

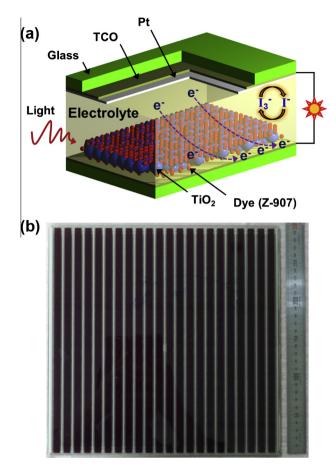


Fig. 1. (a) Schematic diagram illustrating construction of the DSSC module. (b) Fabricated DSSC module consisting of 22 unit cells $(30 \times 30 \text{ cm}^2)$.

sealant. The UV cut film was attached to a TCO glass on the Pt counter electrode side.

2.2. Electrochemical and spectroscopic measurements

The *I–V* characteristics of the module were determined by measuring photocurrent using a Solar Cell *I–V* Tester (Capturestar, Ontest Co., Ltd., Korea) under the simulated solar isolation of AM1.5G generated by a 450 W xenon light source using a Solar Simulation Environmental Chamber (SEC2100, ATLAS, USA) before and after the thermal stability test with a Temp./Humidity Chamber (TS60, SENES, Korea). Raman spectra of the DSSC module before and after the thermal stability test were obtained with a Raman spectrometer (UniRAM, UniNanoTech, Korea) using a 532 nm laser. The laser power was approximately 2 mW and the signal was accumulated for 30 s.

3. Results and discussion

3.1. Electrochemical performance of the DSSC module

Fig. 2(a) presents the photocurrent-voltage curves before and after the thermal stability tests of the DSSC

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