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Improvement in durability of flexible plastic dye-sensitized solar cell modules

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ABSTRACT

Large-area integrated modules of flexible plastic type dye-sensitized solar cell (DSC) have been fabricated based on polyethylene naphthalate (PEN) film for practical applications such as ubiquitous power sources. From the view point of improving durability, composition of organic solvent-based electrolytes has been investigated. As a result, a plastic DSC module using LiI-free electrolyte maintained its energy conversion efficiency of 2% over 220 h under the accelerated condition of 55 °C and 95% relative humidity.

1. Introduction

Reliable durability of dye-sensitized solar cells (DSC) is a key issue for the practical application. DSC modules have been fabricated mainly using glass substrates by AISIN [1], Dyesol (STI Pty. Ltd.) [2], etc., in which mesoscopic TiO_2 electrodes are prepared by high-temperature sintering (>450 °C). Long-term durability of these glass-based cells shows that DSC modules can maintain the output power after several years in outdoor [1]. For commercial application, solar cells should overcome durability tests in accelerated conditions such as 50–85 °C for 1000 h and exposure to continuous solar irradiation (100 mW cm^{-2}). In many cases, the durability of DSC relates to leakage and deterioration of electrolyte, the former being caused by imperfection of sealing process. To overcome these issues, there are many projects replacing organic liquid electrolyte with solid state electrolytes, polymer gel electrolytes, ionic liquid electrolytes, etc. [3–12]. The use of liquid electrolytes with solvents of high boiling temperature (>200 °C), however, is still one of the better solutions improving durability because mesoporous titania film of large surface area can best contact with low-viscosity electrolytic media.

We have been studying plastic film type DSC [13,14]. Lightweight and flexibility are highly sought after especially for consumer electronics. A unique point of our method is using nanocrystalline titania paste for low-temperature coating [15,16]. This paste can form a mesoporous titania film by one-time doctor-blade coating and drying at room temperature. The low-temperature coated and dye-sensitized plastic DSC based on this method exhibit nearly 6% energy conversion efficiency at 1 sun [16]. Our method can also simplify the making of integrated large-area plastic DSC modules. A large full-plastic flexible module of 30 cm × 30 cm has been exhibited in Expo Aichi 2005, and an outdoor durability test was carried out for 1 month [13,14]. After the test, we analyzed the deteriorated DSC module for improving the durability.

We are now building a test production line for plastic DSC modules with low-cost roll-to-roll processes, where a selection of electrolyte is one of crucial points to ensure durability. On taking into account both costs and processes, the use of organic solvents with high boiling temperature is our selection in the first stage. In this paper, we show a part of our results improving durability of plastic DSC, especially by changing electrolyte composition.

2. Experimental

We employed indium tin oxide (ITO) (15 Ω sq^{-1})-coated polyethylene naphthalate (PEN) film (ITO-PEN film; thickness 200 μm; PECF-IP, Peccell Technologies, Inc.), which has sufficiently high resistance against heat and humidity and shows 80% transparency at 550 nm. Fabrication of mesoscopic titania electrode on ITO-PEN followed the previously reported manner, using low-temperature titania coating paste, which can complete coating at room temperature to 150 °C. The resultant film keeps high adhesiveness on ITO-PEN. All the experiments in this paper used N719 dye as a sensitizing dye. Preliminary durability tests

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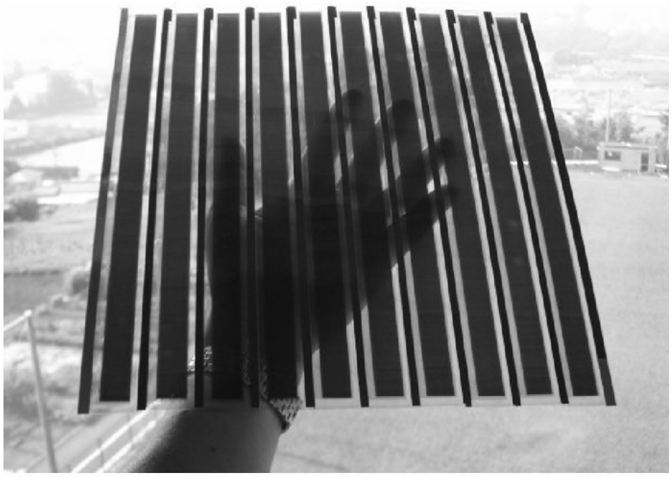

Fig. 1. A flexible full plastic film type DSC, of which titania film is prepared by nanocrystalline titania paste for low-temperature coating.

were carried out by making a miniature cell with an active area size of ca. 6 mm in diameter. Himilan 1702 (thickness 25 μm) and Pt-sputtered F-doped indium tin oxide (FTO) glass were used as a sealing material and counterelectrode, respectively, for the miniature cell.

A large-area plastic DSC of square 30 cm × 30 cm with series connection of 10 unit cells on a flat flexible film was fabricated as shown in Fig. 1. For DC connections (integration), long strip-shaped unit cells with a size of 3.5 cm × 30 cm were connected at the long side with a double-stick conductive tape. On the both edges of long side of a unit cell, conductive Ag grids for current collection were mounted at a temperature less than 120 °C. Usually, low-temperature printing of Ag grid on ITO surface causes high contact resistance between Ag and ITO. However, we improved the Ag paste and coating process to minimize the contact resistance. As for sealing materials for large-area modules, a hot-melt type sealer, which is still in development, was used for preventing electrolyte from leakage. Heat sealing was done at around 120 °C, giving a rubber-like flexible seal, which can follow flexible ITO-PEN. Preparation methods for semi-transparent flexible plastic counterelectrodes by sputtering Ti/Pt alloy, coating a paste consisting of PEDOT-PSS, and coating nano-carbon-based materials have been reported elsewhere [10,11,17,18]. The module shown in Fig. 1 employed the Ti/Pt alloy-based counterelectrode.

Electrolyte composition, which gives highest efficiency for plastic DSCs with low-temperature coating paste, is as follows: LiI 0.4 M, I_2 0.04 M, tetrabutylammonium iodide 0.4 M, *N*-methylbenzimidazole 0.3 M in a mixture of methoxypropionitrile (MPN) and acetonitrile in 1:1 (electrolyte A in Table 1).

I–V characteristics were measured by a source meter (Keithley 2400) controlled by an original software under irradiation of a solar simulator (PEC-L11, Peccell Technologies, Inc.) or real sunshine. AC impedance spectra were measured by Princeton VSP/Z-01 in a frequency range from 20 kHz to 1 Hz. Espec SH-221 was used in preservation storage tests of miniature cells at constant temperature and humidity.

3. Results and discussion

The 10-cell DC module (Fig. 1) was exhibited outdoor in EXPO 2005 Aichi for 1 month. The module showed a maximum efficiency of about 2% under irradiance of 0.3 sun (1 sun = 100 mW cm^{-2}) and maintained its basic photovoltaic activity after 1 month outdoor as shown in Fig. 2; however, it underwent deterioration in photocurrent and fill factor by exposure to rain, temperature change and UV light. An electrolyte composition used was LiI 0.4 M, I_2 0.04 M, tetrabutylammonium iodide 0.4 M, 4-*tert*-butylpyridine, *N*-methylbenzimidazole 0.3 M in a mixture of MPN and γ-butyrolactone (GBL) (1:1) (electrolyte B in Table 1), where GBL was used to improve durability of the cell due to its relatively high boiling temperature, 203 °C. After the 1-month exposure no electrolyte leakage occurred. However, the titania film partially came off from the ITO plastic substrate. Furthermore, we found that a large amount of ITO conductive layer was lost probably due to chemical etching reaction.

Table 1
Electrolyte compositions of plastic DSC for investigating causes of deterioration of ITO

	I_2	LiI	TBAI	NMB	Solvent
A	0.04	0.4	0.4	0.3	AN/MPN
B	0.04	0.4	0.4	0.3	GBL/MPN
C	0.04	0.4	0.4	0	GBL/MPN
D	0.04	0.4	0	0.3	GBL/MPN
E	0.04	0	0.4	0.3	GBL/MPN

Unit: mol L^{-1}: I_2: iodine; LiI: lithium iodide; TBAI: tetrabutylammonium iodide; NMB: *N*-metylbenzimidazole; AN: acetonitrile; MPN: methoxypropionitrile; GBL: γ-butyrolactone.

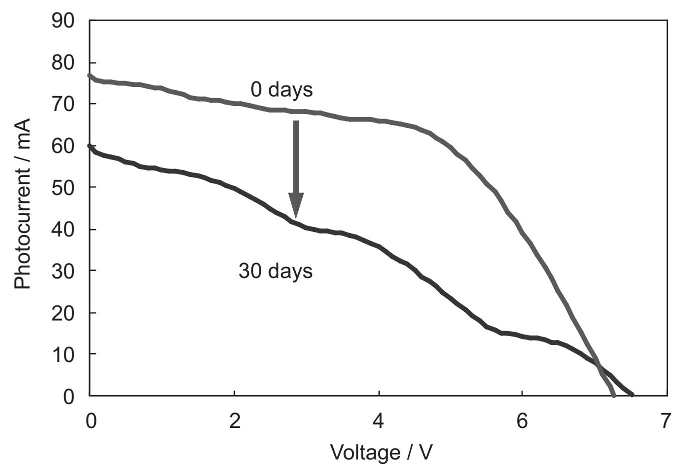

Fig. 2. Change in *I–V* curve of a plastic DSC module exhibited in EXPO Aichi. Irradiance was 0.3 sun (1 sun = 100 mW cm^{-2}).

In order to know causes of disappearance of ITO from the surface of ITO-PEN in the plastic DSC after 1-month outdoor durability test, we did durability test using various kinds of electrolyte compositions. Table 1 shows some examples of electrolyte compositions that were tested. It is well known that ITO has a low chemical stability especially against both strong acid and alkaline solutions, indicating that composition of electrolyte directly affects durability of plastic DSC using ITO. The optimal electrolyte composition for plastic DSC seems to differ from that for conventional DSC using the FTO glass. The usage of ITO, unlike FTO having high chemical stability, is a key difference between glass DSC and plastic DSC. With plastic DSC, we have to take care so as not to damage ITO by chemical reasons.

Electrolyte B was applied in the module exhibited in Expo 2005, which damaged ITO as mentioned. Electrolytes C, D and E are alternatives where one component is removed from electrolytes A and B. DSCs made with electrolytes B, C, D and E were kept in a constant temperature and humidity chamber under the condition of 55 °C and 95% RH. In order to check ITO deterioration, the *I–V* characteristics and AC impedance spectra were investigated.