Quasi-Solid-State Dye-Sensitized Solar Cell with Ionic Polymer Electrolyte

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A quasi-solid-state dye-sensitized solar cell fabricated with ionic polymer electrolyte showed a 3.8% conversion efficiency under AM 1.5 (100 mW cm^{-2}) irradiation, and long-term stability without any sealing.

Dye-sensitized solar cells have attractive feature in high photon-to-current conversion efficiency and low production cost.[1] These cells typically employ a liquid electrolyte to regenerate the dye. The use of a liquid electrolyte in dye-sensitized solar cells compromises their long-term durability and stability due to, for example, evaporation or leakage of the solvent and difficulty in robust sealing. Solution of such stability issues is important for the commercialization of this technology. To address this problem, attention is increasingly focusing on developing solid materials replacements of the liquid electrolyte, where organic and inorganic hole conductors,[2] polymer electrolytes,[3] and addition of gelators in the liquid electrolyte[4] are discussed. Recently, we succeeded in constructing a quasi-solid-state cell with ionic liquid and low molecular weight gelator,[5] achieving the high temperature stability, but the cell required tough sealing because of its relatively low gel-to-solution transition temperature. In our previous report, poly(hexa(oxyethylene)methacrylate) (MHH) was employed to obtain thermo-irreversible chemical gel in organic liquid electrolyte of dye-sensitized solar cell.[3c] However, problems of stability or sealing still remain due to inclusion of organic solvent in the electrolyte. Here, we report preparation and application of ionic polymer electrolyte to quasi-solid-state dye-sensitized solar cell without any sealing and discuss stability of one.

TiO_2 film (area = 0.25 cm^2) was obtained by coating a TiO_2 paste (d = 12 μm, Ti-Nanoxide TSP, Solaronix) and diffracting layer[6] (d = 4 μm, HPW300C, Catalysts & Chemicals Ind. Co.) on a conducting glass (10 ohm square^{-1} F doped SnO_2, Nippon Sheet Glass) with screen printing technique. Dye (Ruthenium TBA 535, Solaronix) adsorption was carried out as reported procedure.[4a] The cells with ionic polymer electrolyte (IPE) were prepared as follows; a monomer MHH (Blemer 350, NOF) and AIBN dissolved in 1-hexyl-3-methylimidazolium iodide (Shikoku Corp.) was applied on dye-adsorbed TiO_2 film. In situ polymerization was performed by heating the solutions at 80 °C for 12 h. After polymerization, I_2 was introduced by sublimation in a closed container (vol. 97 mL, I_2 0.08 g) at 30 °C. The amount of I_2 introduced to the electrolyte was controlled by sublimation time.[3b] A poly(3,4-ethylenedioxythiophene) film[7] coated conducting glass as counter electrode (CE) was pressed to the gel electrolyte. As a reference, organic solvent electrolyte (OE) prepared using 0.6 M of 1,2-dimethyl-3-propylimidazolium iodide, 0.1 M (1 M = 1 mol dm^{-3}) of LiI, 0.05 M of I_2 and 0.5 M of 4-*tert*-butylpyridine dissolved in methoxyacetonitrile, ionic liquid electrolyte (IE) with the same composition to IPE without MHH and AIBN were used. Photoenergy conversion efficiency was evaluated under AM 1.5 irradiation (100 mW cm^{-2}, from a solar simulator, YSS-80 Yamashita Denso). Cell performance was described as the average of at least 3 samples. The amount of I_2 introduced in the electrolyte was determined by absorbance of I_3^- at 360 nm extracted from the electrolyte with acetonitrile ($\varepsilon = 2.55 \times 10^4$ M^{-1} cm^{-1}).[8] Gelation test was carried out by upside-down test tube method.[9]

Higher concentration of MHH in the electrolyte gave higher mechanical strength of polymer gel, but decreased its conductivity[10] and non-flammability. To minimize the concentration of monomer and initiator to obtain highly conductive and non-flammable gel electrolyte, gelation test was carried out (Table 1). Poly(MHH) showed excellent compatibility, and gave transparent gel at the concentration above 5% for MHH and 1% for AIBN.

Table 1. Gelation test at various concentrations of MHH and AIBN

		[AIBN]/wt.%		
		0.5	1	2
[MHH] /wt.%	3	×	×	×
	5	×	○	○
	10	○	○	○

○ gel, × liquid

In this system, I_2 was added after polymerization to avoid quenching of radical polymerization. Figure 1 shows conversion efficiency with increasing I_2 introduced to the ionic polymer electrolyte. The efficiency increased with increasing the amount

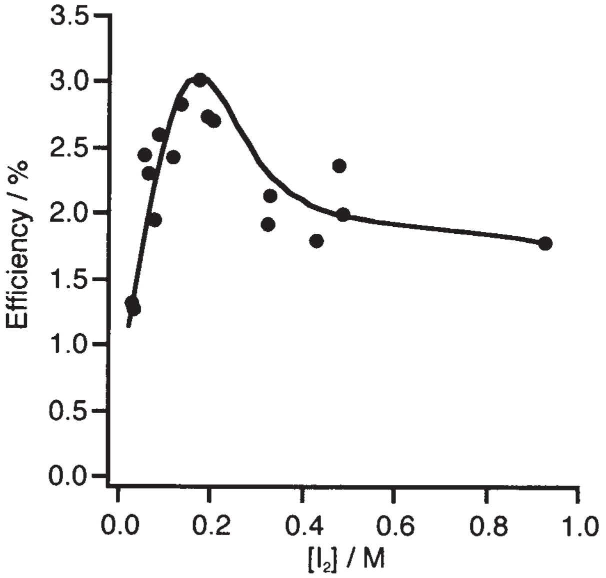

Figure 1. Effect of concentration of iodine on efficiency for IPE cell.

of I_2 introduced up to 0.2 M, and gradually decreased at higher concentration. Photocurrent, which is proportional to efficiency, was restricted by supply of I_3^- to CE at 100 mW cm^{-2} irradiance at low I_2 concentration, and also limited by absorption of incident photon and back electron transfer to I_3^- at high I_2 concentration.[11] As a result, the efficiency showed a maximum value at 0.2 M.

Figure 2 shows photocurrent-voltage curves of the cell with IPE, IE, and OE under AM 1.5 irradiation. V_{OC}, J_{SC}, fill factor (FF) and efficiency (η) of the cells were listed in Table 2. The result implies that the poly(MHH) should build up a network structure with little inhibition of the charge transport, even in ionic liquid electrolyte as we observed in organic electrolyte solutions.[5] The conversion efficiency obtained from ionic polymer electrolyte cell was ca. 2/3 of OE cell.

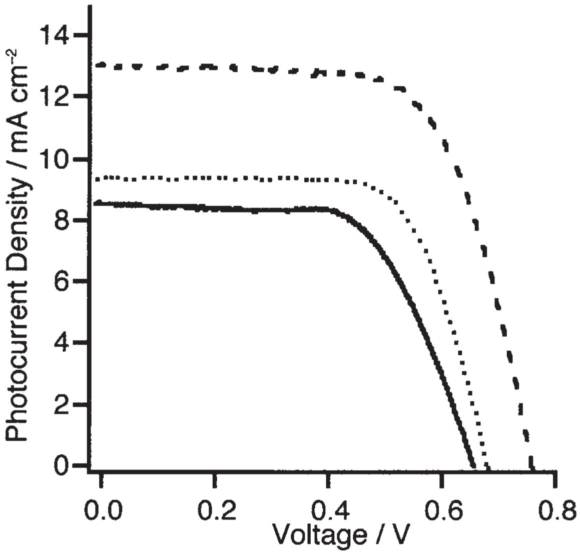

Figure 2. Photocurrent-voltage curves of the cells with ionic polymer electrolyte (IPE: solid curve), ionic liquid electrolyte (IE: dotted curve), and OE (dashed curve) under AM 1.5 (100 mW cm^{-2}) irradiation.

Table 2. Cell performance of the dye-sensitized solar cell

electrolyte	Area/cm^2	V_{OC}/V	J_{SC}/mA cm^{-2}	FF	η/%
IPE	0.25	0.66	8.6	0.66	3.8
IE	0.25	0.68	9.4	0.69	4.4
OE	0.25	0.76	13	0.66	6.5

The ionic polymer cells showed excellent durability without any sealing. Figure 3 shows time-dependent change in the photoconversion efficiency of IPE and IE without any sealing, and OE with simple sealing using epoxy resin. Efficiency of the OE cell decreased immediately due to the solvent evaporation, but the IPE cell kept 90% of the initial efficiency even after 80 days at r.t., because it contains no volatile solvent.

Using of a non-volatile and non-flammable electrolyte composed of ionic polymer electrolyte provides a practical efficiency and stability of dye-sensitized solar cell without any sealing.

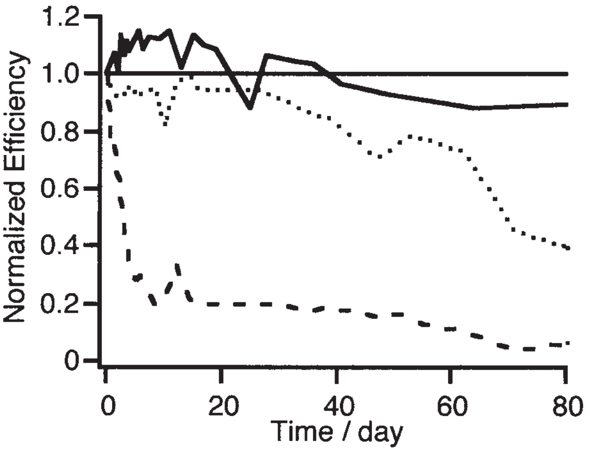

Figure 3. Time-course change of the normalized conversion efficiency of the solar cells stored at r.t.; with IPE (solid curve), IE (dotted curve), and OE (dashed curve).

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