Fabrication of Quasi-solid-state Dye-sensitized TiO_2 Solar Cells Using Low Molecular Weight Gelators

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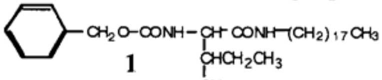
Low molecular weight gelators were applied to solidify the redox electrolyte in dye-sensitized TiO_2 solar cells. The resulting quasi-solid-state dye-sensitized solar cells showed comparable efficiency and higher stability than the similar cell with the liquid phase redox electrolyte.

Novel solar cells constructed using dye molecules as photosensitizers, nano-structured TiO_2 as the electron-transport layer and a redox electrolyte as the "hole-transport layer" have attracted much interest because of their low cost, high efficiency and earth-friendly characteristics.[1] The hole-transport layer consists of a mixture of organic solvents such as ethylene carbonate and acetonitrile, and an electrolyte containing a redox couple, e.g., I^-/I_3^-. The major remaining problem of the dye-sensitized p-n porous-junction solar cell is the stability of the liquid-phase hole-transport layer, because the liqid hole-transporting electrolyte often causes problem of leaks in long-term operation due to difficulty in the hermetic sealing of the module. Several attempts were made to improve long-term stability using p-type semiconductors,[2] room temperature molten salts,[3] ionic conducting polymers,[4,5] or conducting organic polymers[6] as a hole-transport layer. However, the efficiencies of the cells were found to be unsatisfactory compared to those using the organic liquid phase redox electrolyte.

In the quasi-solid-state solar cells using ionic conducting polymers, the module fabricated by gelation of the liquid-phase hole-transport layer using polyacrylonitirle was worth noting. However, the low incident photon-to-current conversion efficiency of the module was observed and explained as due to incomplete wetting of the nano-structured TiO_2 film by the polymer gel electrolyte.[4] Consequently, sophisticated gelation of the liquid-phase hole-transport layer seems to be promising as quasi-solidification of the module. Recently, some amino acid derivatives with phenyl and alkyl groups were found to work as gelators for the liquid phase organic electrolytes at the very low concentration.[7] Interestingly, the behavior of supporting electrolytes in the resulting organogel is essentially similar to that in the isotropic solution, and the ionic mobility of supporting electrolytes is scarcely affected by the gelling molecules. With these facts in view, we successfully attempted gelation of the liquid-phase hole-transport layer using such amino acid derivatives.

The dye-anchored porous TiO_2 electrode was prepared using the N3 dye, *cis*-di(thiocyanato)-N,N'-*bis*(2,2'-bipyridyl-4,4'-dicarboxylic acid)ruthenium(II) complex, commercial available P25 TiO_2 (Nippon Aerosil), and a fluorine-doped SnO_2-layered glass (OTE) (sheet resistance of 10 Ω/cm^{-2}, Nippon Sheet Glass, Japan) as reported previously.[8] The dye-anchored TiO_2 electrode was combined with platinum-coated OTE glass electrode by employing the adhesive films (HIMILAN 1652, Mitsui-Dupont Polychemical, Japan) to make ca. 30 µm gap between the electrodes. The following amino acid derivatives, **1**, **2**, **3**, were synthesized as reported previously[7] and used as low molecular weight gelators.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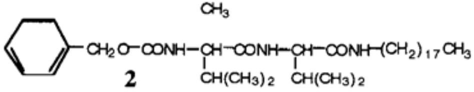
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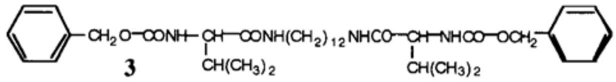
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A typical procedure of gelation is as follows; a weighed gelators (0.1 M) was mixed with a methoxy-propionitrile solution containing lithium iodide (0.1 M), 1,2-dimethyl-3-propylimidazolium iodide (0.6 M), iodine (0.1 M) and 4-*tert*-butylpyridine (1 M). The mixture were dissolved by heating up to 100-140 °C, and the resulting fluid electrolyte was introduced through an injection part of the combined electrode which was kept at ca. 80 °C on hot-plate. After the injection of the fluid electrolyte, gelation of the cell was carried out by cooling down to 25 °C. The injection part of the quasi-solid-state cell was sealed using paraffin wax instead of epoxy resin in order to evaluate vaporization of organic solvent in short time period. For comparison, the solar cell without using any gelators was also fabricated and sealed in the same way. Photoelectrochemical measurements were performed using AM 1.5 solar simulator (YSS-80: Yamashita Denso Co.) as a light source, and computer controlled digital multimeter (model 166; Keithley, model HP3478A; Hewlett-Packard) to measure photocurrent and voltage.[5]

Use of the gelators resulted in the formation of optically transparent gel-electrolyte. Figure 1 shows photocurrent-voltage

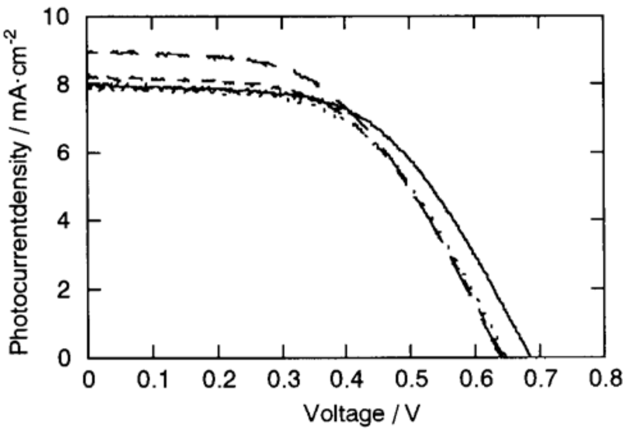

Figure 1. Photocurrent-voltage characteristics of the quasi-solid-state solar cells; with gelator **1** (long dash line), **2** (short dash line), **3** (dotted line), and without gelator (solid line).

Table. Characteristics of the quasi-solid-state solar cells

system	V_{OC} / V	i_{SC} / mA cm^{-2}	FF	η / %
Liquid	0.68	8.0	0.55	3.0
1	0.64	9.0	0.53	3.0
2	0.64	8.2	0.55	2.9
3	0.65	7.8	0.56	2.8

characteristics of the fabricated quasi-solid-state solar cells using gelators, **1**, **2**, **3**, respectively. Open circuit voltage (V_{OC}), short-circuit photocurrent (i_{SC}), fill-factor (FF), and photoenergy conversion efficiency (η) of the cells were listed in Table. Compared to the liquid-phase solar cell fabricated without using any gelators, the quasi-solid-state solar cells gave comparable or larger values of i_{SC} and slightly decrease in V_{OC} by 30 - 40 mV. Surprisingly, the values of FF and photoenergy conversion efficiency were found comparable each other under AM 1.5 light irradiation. The quasi-solid-state solar cells also showed no decrease of the conversion efficiency in the light intensity ranging from 10 to 100 mW cm^{-2}.

These observation and facts indicate that the low molecular weight gelators successfully build up the three-dimensional gel structure which may support the redox couple (I^-/I_3^-) solution without decreasing their hole-transport activity. The gelators should induce macromolecular-like aggregates and intertwining of the aggregates through intermolecular hydrogen bonding of amide groups and van der Waals interactions of alkyl chains.[7] Accordingly, the formation of such molecular aggregate are not affected by the redox electrolytes in the system and then, the low molecular weight gelators hardly interferes with the ionic mobility of the redox couple, I^-/I_3^-. In other words, the employed low molecular weight gelators can induce gelation of the hole-transport layer without lowering the hole-transport activity.

Melting points of the gelators, 1, 2, 3, are 61.5, 78.5, 66.8 °C, respectively. They gave relatively low viscosity of the gel electrolyte solutions when they are heated up to higher temperature than their melting point (**1** at 110 °C, **2** and **3** at 140 °C). The low viscosity of the fluid electrolyte solution at 80 °C would also contribute to the effective diffusion of the redox ionic species into the nano-space, leading to the successful fabrication of the uniform hole-transport layer in the porous dye-coated TiO_2 solar cells.

As expected, the gelation also contributes to the maintenance of the efficiency of the solar cells through suppression of vaporization of solvent molecules from the hole-transport layer. Figure 2 shows a time-course changes in the photoconversion efficiency of the fabricated solar cells. The liquid phase solar cell lost the photoconversion efficiency in two days because organic solvent should leak from the electrolyte layer due to the paraffin wax sealing (instead of epoxy resin sealing) of the injection part. Use of the gelator resulted in improvement of the stability of the solar cells under the comparable conditions. The improvement was apparent in the case of gelators 2 or 3 rather than 1, which should be attributed to the difference in the number of amide groups. The gelators with many amide groups would slow down the evaporation of solvent molecules by immobilizing in the more tight three-dimensional network.

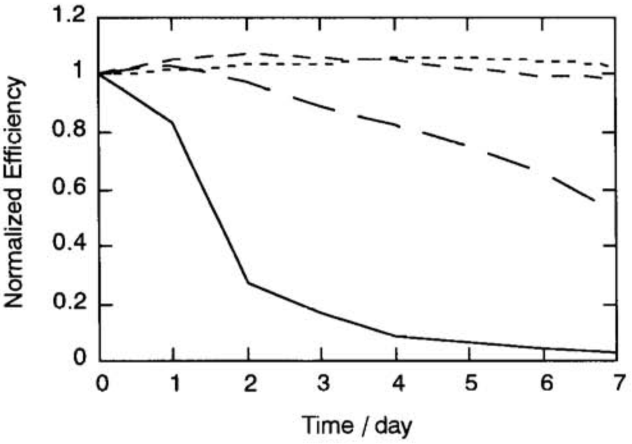

Figure 2. Time-course change of the normalized photoconversion efficiency of the quasi-solid-state solar cells; with gelator **1** (long dash line), **2** (short dash line), **3** (dotted line), and without gelator (solid line).

In conclusion, the gelatinized hole-transport layer was demonstrated for the first time to have comparable characteristics as the liquid phase hole-transport layer. The low molecular weight gelators can induce uniform and effective gelation of hole-transport layer of I^-/I_3^- in the dye-coated TiO_2 network, retarding evaporation of organic solvent molecules from the liquid phase in the networks.

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