Dye-sensitized Solar Cell with Polysaccharide Solid Electrolyte

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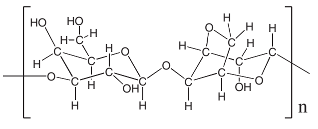
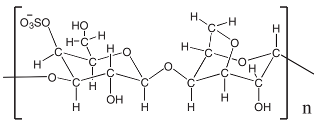
A solid state dye-sensitized solar cell was successfully fabricated using inexpensive polysaccharide solid involving redox electrolyte and organic medium with the incident photon-to-electricity conversion efficiency over 7%.

The photosensitized solar cell composed of nanoparticulated TiO_2 porous film adsorbing dye reported by Graetzel's group[1] has shown a great success in the relevant research area. This so-called Graetzel's cell has reported to give nearly 10% conversion efficiency under AM 1.5 solar irradiation with high cost-performance, and so is attracting a great deal of attention as a future commercial solar cell. One of the problems of this cell to be solved for practical use is that it uses organic liquid. To overcome this problem solidification of the organic redox electrolyte solution by molten salts and gelator[2] or by polymer film[3] has been achieved. Another approach is to use water,[4,5] but the efficiency and stability of the cell in an aqueous phase have been low.

The present authors have reported that polysaccahrides such as agarose (**1**) and κ-carrageenan (**2**) can form a tight and elastic solid containing excess water, and that electrochemical and photochemical reactions can take place in the solid the same as in pure water.[6] The hardness of the solid is, for instance, almost the same as a brick cheese and one third of a conventional rubber eraser for a 2 wt % κ-carrageenan solid involving excess water. We have expected that such an interesting solid containing a large excess liquid could offer a solid state medium for the photosensitized cell. We have succeeded in substituting the water in the solid with organic liquid, and have found that this solid involving organic solvent and I^-/I_3^- redox electrolyte works well as a medium for the TiO_2 cell with a well-known N3 dye sensitizer.



1 (Agarose)



2 (κ-carrageenan)

A colloidal aqueous solution of P-25 (received from Japan Aerosil Co. Ltd.) was spin-coated on an ITO electrode (1.0 × 2.0 cm) and heated at 100 °C for 30 min. This procedure was repeated several times and then finally the TiO_2 coated ITO was heated at 450 °C for 30 min to prepare a nanoporous TiO_2 thin film of 10 µm thickness. This ITO/TiO_2 film was soaked in a 1.5×10^{-4} M ethanol solution of *cis*-bis(isothiocyanato)bis(4,4′-dicarboxyl-2,2′-bipyridine)ruthenium(II), $Ru(dcbpy)_2(NCS)_2$ (called N3) to adsorb the complex onto the TiO_2. A 2 wt % κ-carrageenan (purchased from Wako Pure Chemical Ind. Ltd.) was dissolved in water by applying very carefully a high frequency wave (2.45 GHz). Before solidifying the solution was poured onto the TiO_2/N3 film and solidified by cooling down to room temperature. $(C_3H_7)_4NI$ and I_2 (10:1) were dissolved in a mixture of acetonitrile and 3-methyl-2-oxazolidinone (1:1) so that their concentrations become 0.3 M and 0.03 M, respectively, and the water in the carrageenan solid on the TiO_2/N3 film was substituted by the mixture solution by pouring the mixture onto the TiO_2/N3/carrageenan solid film. As for the counter electrode, a 5 mM H_2PtCl_6 ethanol solution was spin-coated on an ITO electrode plate, and then the coated ITO was heated at 450 °C for 1 h to prepare a transparent Pt-coated ITO. The ITO/TIO_2/N3/solid (involving organic liquid with $(C_3H_7)_4NI$ and I_2) working and the ITO/Pt counter electrodes were put together to fabricate a dye-sensitized cell. The effective area of the TiO_2 was 0.4 × 0.5 cm (0.20 cm^2). This cell was irradiated from the TiO_2 side with a 98 mWcm^{-2} visible light from a 500 W xenon lamp using a Toshiba. L-42 and IRA-25S cutoff filters.

The I–V characteristics of the cell is shown in Figure 1, and the results are summarized in Table 1 where the performance of the cell composed of the corresponding liquid medium is also given with the same conditions as the solid state cell.

In the Table 1 short circuit photocurrent (J_{sc}), open circuit photovoltage (V_{oc}), Fill Factor (ff) and light-to-electricity conversion efficiency (η) are given. In the Run 3 the TiO_2/dye electrode was treated with a 2 mol% *tert*-butylpyridine/acetonitrile solution before cell fabrication in order to suppress back electron transfer from the injected electron into the TiO_2 to the oxidized dye. In the Runs 4 and 5, a 0.5 M *tert*-butylpyridine solution was added in the cell medium, and fluorine-doped NESA conductive glass was used for the base electrode. Although optimum conditions were not investigated, the solid-state cell showed always even better performance than the corresponding conventional (reference) liquid type cell. The details should be investigated in future.

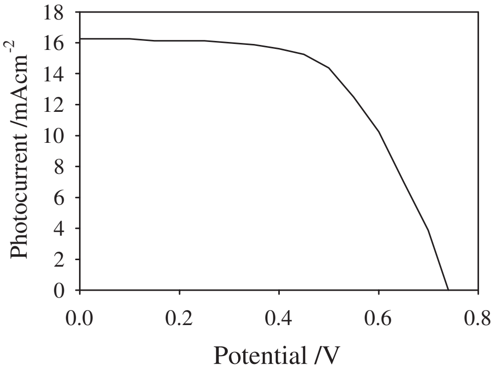


Figure 1. I–V curve of the solid-state dye-sensitized solar cell, TiO_2/N3/Carrageenan solid involving acetonitrile/3-methyl-2-oxazolidinone (1/1) and $(C_3H_7)_4NI/I_2$(0.3 M/0.03 M)/Pt. The data correspond to Run 4 of Table 1.

Table 1. Solid-state dye-sensitized solar cell, TiO_2/N3/Carrageenan solid involving acetonitrile/3-methyl-2-oxazolidinone (1/1) and $(C_3H_7)_4NI/I_2$(0.3 M/0.03 M)/Transparent Pt.

Run	Electroyte medium	J_{sc}/mA cm^{-2}	V_{oc}/V	ff	η/%
1	Liquid	13.75	0.68	0.46	4.39
2	Solid	13.50	0.68	0.51	4.82
3[a]	Solid	17.50	0.71	0.41	5.22
4[b]	Solid	16.25	0.72	0.61	7.23
5[b]	Liquid	13.25	0.76	0.56	5.42

[a] TiO_2/N3 was treated with 2 mol% *tert*-butylpyridine/acetonitrile solution before cell fabrication. [b] 0.5 M *tert*-butylpyridine was added in the solution; fluorine-doped NESA and Pt plate were used for working and counter electrodes. Runs 1/2 and Runs 4/5 are comparable, respectively.

In the present cell system a transparent Pt-coated ITO counter electrode was used for the Runs 1 and 2 in the Table 1. The transmittance of the counter electrode was 40% at 400 nm and 70% at 800 nm, with average transmittance of about 60% between 400 and 800 nms, which would allow usage of another cell behind it when a cell capable of absorbing longer wavelength light was developed in future. The diffusion coefficient of holes via the I^-/I_3^- redox couple in the solid involving 2.5 wt % carrageenan, 0.3 M KI and 0.03 M I_2 and excess water was investigated by an impedance spectroscopy:

It was ca. 1.7×10^{-5} cm^{2}s^{-1}, almost the same as in a liquid water showing that the hole transport in the solid is not problem in comparison with the liquid medium system. In the present solid transport of small ions and molecules takes place the same as in a liquid showing that the liquid phase in this solid behaves as in a pure liquid. The details are now under investigation.

As for the polysaccharide concentration, more dilute one (e.g., 0.5 wt %) gave higher conversion efficiency, and more concentrated one (3 wt %) gave worse results. The adsorbed dye was usually in the order of 8×10^{-8} mol cm^{-2}, but the distinct effect of the coverage was not found yet. These are the factors to be investigated in future.

Polymer gels are usually soft and fragile. However, the present solid is hard and elastic as mentioned before. Although a long-term performance was not tested yet, the photocurrent did not decrease after 4 h irradiation.

Thus, a solid-state dye-sensitized solar cell was easily fabricated by using an inexpensive polysaccharide solid involving organic medium and I^-/I_2 redox electrolyte.

References

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