Development and characterization of the dye-sensitized solar cells using solid polymer electrolytes

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Solid-state dye-sensitized solar cells were fabricated using solid polymer electrolyte consisting of the hyper-branched graft copolymers of poly(methyl methacrylate–co-chloromethlystyrene)-g-poly[(oxy-ethylene)$_9$ methacrylate] (PMMA-g-POEM$_9$) synthesized by atom transfer radical polymerization (ATRP) and I^-/I_3^- redox couple supporting electrolyte. The photoelectrochemical performances of these solar cells are investigated. For the polymer electrolyte, the short circuit current density (I_{sc}) and the open circuit voltage (V_{oc}) obtained for an incident light intensity of 110 mW cm^{-2} were 0.196 mA cm^{-2} and 0.503 V, respectively. This corresponds to an overall efficiency to electric energy conversion efficiency (η) and fill factor (ff) of 0.053 % and 0.593,respectively. The low efficiency for energy conversion, in comparison to cells with liquid electrolytes, was attributed to the reduced mobility of I^-/I_3^- in polymer electrolyte and the poor electric contact between polyelectrolyte and porous thin film electrode. For the improvement of the performance, the heating treatment of solar cells and the adherence of solid polymer electrolyte by the electrochemical deposition of ZnO film were examined.

Key Words: dye-sensitized solar cell, solid polymer electrolyte, electrodeposition, branched graft polymer

1. INTRODUCTION

Dye-sensitized solar cells (DSCs) based on porous semiconductor film modified by the dye molecules have considerable attention, since O'Regan and Grätzel reported especially high conversion efficiency approaching 10%.[1-3] After that, there have been various attempts to improve the cell performance. The electrolyte usually used in these cells is an I^-/I_3^- redox couple in a mixture of ethylene carbonate and propylene carbonate. In dye-sensitized solar cells using liquid electrolytes, major problems are difficulty in sealing, leakage of liquid electrolytes and less long-term stability. The solid-state dye-sensitized solar cell with solid polymer electrolyte (SPE) based on poly (epichlorohydrin-co-ethylene oxide) has been assembled by Paoli.[4] However the overall conversion efficiency of the cell was found to be only 0.22%. This may be related to the low conductivity of the electrolyte and the imperfect contact between the polymer electrolyte and nanocrystalline TiO$_2$ film electrode.

In previous sutdy,[5] the solid polymer electrolyte made from a hyper-branched graft copolymer, that was synthesized by atom transfer radical polymerization (ATRP). This polymer is consisting of covalently-bonded two chemically different polymer segments. One of the polymer segments have high glass transition temperature (T$_g$) led to high mechanical strength. The other segment has low T$_g$ and high solubility of supporting electrolyte led to high electric conductivity. A macroinitiator of poly(MMA-co-CMS)

for ATRP is prepared by copolymerization of methyl methacrylate (MMA) and chloromethlystyrene (CMS). A hyper-branched graft copolymer of PMMA-g-POEM$_x$ is synthesized using ATRP by grafting POEM$_x$ side chains on the macroinitiator.

In this study, the solid-state dye-sensitized solar cell, using the solid polymer electrolyte consisting of the hyper-branched graft copolymer and I^-/I_3^- redox couple supporting electrolyte was produced and evaluated their photoelectrochemical performance. The polymer electrolyte was applied to the solar cell using ZnO/N3 hybrid thin film electrode prepared by the electrodeposition method.

2. EXPERIMENTAL

2.1 Preparation of TiO$_2$ dye-sensitized electrodes

Nanocrystalline TiO$_2$ films were prepared by spreading a viscouse dispersion of TiO$_2$ powder with water and ethyl alcohol mixture solution on a conduction glass support (Asahi FTO glass, fluorine-doped SnO$_2$ overlayer, transmission >85% in the visible sheet resistance 10 Ω /square) with heating for 30min at 450 ℃ . Nanocrystalline TiO$_2$ films (20 μ m thick) were coated with ruthenium complex N3 dyes, Ru(dcbpy)$_2$(NCS)$_2$ (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine), by immersion the film into 5.0 × 10^{-4} mol dm^{-3} N3 solution in *tert*-butylalcohol. The N3 dye was purchased from Kojima Chemicals Co., Ltd. (Saitama, Japan). The dye-coated TiO$_2$ electrode was incorporated into thin-layer sandwich-type cell with a Pt sputtered FTO as
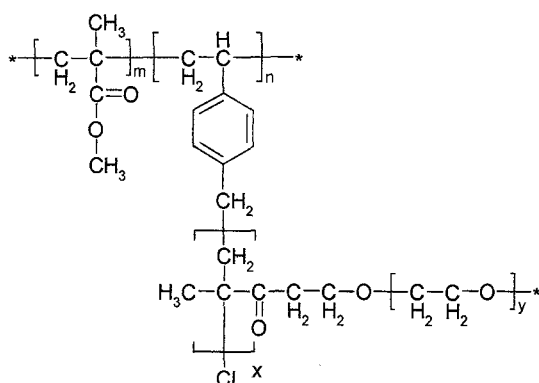
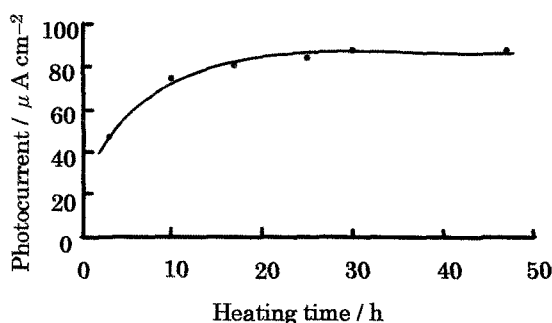Fig.1 Chemical structure of the hyper-branched graft copolymer poly(MMA-g-POEM$_x$).

Fig.2 Photocurrent-time plot for solid dye solar cell taken from heat treatment at 90℃.

the counter electrode, spacer film, and electrolyte to measure the solar cell performance. The liquid electrolytes were 0.1 mol dm^{-3} I$_2$ and 0.01 mol dm^{-3} LiI in acetonitrile solution.

2.2 Preparation of ZnO dye-sensitized electrodes.

The preparation of ZnO/N3 hybrid electrode for the DSCs was carried out due to the work by S. Karuppuchamy et.al.[6-8] The N3 dye was stocked as aqueous solution dissolved in a 0.1 mol dm^{-3} NaOH solution and adjusted at pH 6 by adding appropriate amounts of HCl solution. The deposition bath was prepared by mixing the dye solution with aqueous solution of Zn(NO$_3$)$_2$ at an appropriate ratio to get the final concentrations of 100 μ mol dm^{-3} N3 and 0.5 mol dm^{-3} Zn(NO$_3$)$_2$. The ZnO/N3 hybrid film were deposited by potentiostatic electrolysis at -1.0 V (vs. Ag/AgCl) for 60 minutes. The deposited electrode were dried in air at room temperature and used to further experiments without any heat treatments.

2.3 Preparation of dye- sensitized solar cells

The solid polymer electrolyte was made by casting an acetone solution of hyper-branched graft copolymers, 0.1 mol dm^{-3} I$_2$ and 0.01 mol dm^{-3} LiI on the dye-coated TiO$_2$ electrode and by drying it at 90℃ for 24 hour.

A macroinitiator of poly(MMA-co-CMS) for ATRP was prepared by copolymerization of methyl methacrylate (MMA) and chloromethylstyrene (CMS) by a conventional radical polymerization. MMA/CMS composition was measured by nuclear magnetic resonance spectra using spectrometer for ^{1}H (JEOL JNM-EX270 FT NMR system). The hyper-branched graft copolymer was synthesized using ATRP by grafting POEM$_9$ side chains on the macro-initiator. The chemical structure of the hyper-branched graft copolymer is shown in Fig.1. The preparation and characterization of hyper-branched grafting copolymer was carried out in a manner similar to the previous paper.[5]

2.4 Electrochemical measuerments

The photovoltage and photocurrent were measured with the potentio/galvanostat HA-303 (Hokuto Denko Co., Ltd., Tokyo, Japan), function generator HB-104 (Hokuto Denko Co., Ltd., Tokyo, Japan) and X-Y recorder F-35A (Riken Denshi Co., Ltd., Tokyo, Japan). The light source was halogen lamp (100V, 300W) focused to 110 mW cm^{-2}. Intensity of the incident light was checked with hign sensitivity spectro multichannel photodetector MCPD-7000 (Otsuka Electronics Co., Ltd., Osaka, Japan), by placing the prove of the radiometer in front of the incident light at the same distance, where the solar cell is placed.

3. RESULTS AND DISCUSSION

3.1 Conjugation solid polymer electrolyte to nanocrystalline TiO$_2$ film electrode

In generally, the various battery cells using the solid polymer electrolyte indicates low power outputs. A part of the reason is the lower composition surface area between solid polymer and surface of electrode, because of the viscosity of a solid polymer and/or a solid polymer solution. For the improvements of the conjugation, the sandwich-cell using solid polymer electrolyte produce an increase in temperature at 90℃ in heat incubator. The result is shown in Fig.2. The MMA/CMS ratio and POEM$_9$ content were 107 and 51 %(w/w),respectively. In this result, the photocurrent increases with increasing heating time to 25 hour, above which it stay constant. It is known that the calcinations of TiO$_2$ powder was not observed at this temperature. It means that the solid polymer electrolyte was introduced into deep part of nanocrystalline TiO$_2$ films, because of the permeation of melted solid polymer electrolyte. On the observation of photoelectrode, the back side of electrode was colored to brown with increasing heating time. It indicates the solid polymer electrolyte containing iodide supporting electrolyte was reached into the back of nanocrystalline TiO$_2$ microporous films. Thus, the solid polymer electrolyte can be incorporated into TiO$_2$ films by the use of heating treatment at 90℃ for 25 hour.
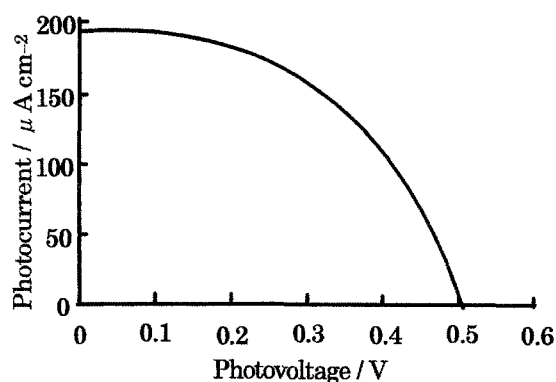
Fig.3 Current-voltage curves of the cells fabricated using 0.027 wt% solid polymer electrolyte solution (10 μ l) containing 0.1 mol dm^{-3} I$_2$ and 0.01mol dm^{-3} LiI.
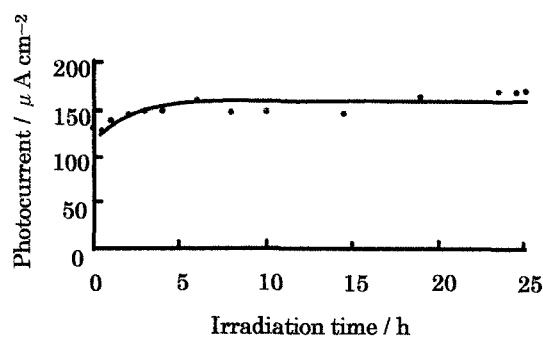

Fig.4 Stability test of solid dye solar cell under 110 mW cm^{-2} halogen light illumination.

3.2 Performance of solid dye-sensitized solar cells

The construction of a solid dye-sensitized solar cells fabricating a sandwich cell using nanocrystalline TiO$_2$ film electrode, solid polymer electrolyte consisting of hyper-branched graft copolymer, and Pt sputtered ITO counter electrode. Figure 3 shows the current-voltage plot measured for a sandwich cell with an active area of 1cm^2 under white light illumination at 110 mW cm^{-2} generated by a filtered halogen lamp. It exhibits a short circuit photocurrent (I$_{sc}$), an open circuit photovoltage (V$_{oc}$), and a fill factor (ff) of 0.196 mA cm^{-2}, 0.503 V and 0.593, respectively. The electric energy conversion

efficiency (η) corresponding to an overall light was 0.053 %. The fill factor (ff) of the dye-sensitized solar cells can be calculated from the equation,

$$ff = P_{max} / (I_{sc} \times V_{oc})$$

where P$_{max}$ is the maximum electrical power obtained. The overall internal light to electricity conversion efficiency is obtainedby the following relationship,

$$\eta = P_{max} / I_s A T$$
$$= I_{sc} V_{oc} ff / I_s T A$$

where I$_s$ is the intensity of illumination, A is the area illuminated and T is the transmittance. The solid polymer electrolyte consisting of the hyper-branched grafting polymer is useable for the electrolyte of dye-sensitized solar cells including iodide redox supporting electrolyte. The improvement of the solid polymer electrolyte cannot be drawn until further experiments.

The photocurrent transients which were measured on the solid dye-sensitized solar cell using suitable polyelectrolyte are shown in Fig.4. The photocurrent of the solid cells under white light illumination at 110 mW cm^{-2} increases gradually up to 0.165 mA cm^{-2}, from then of 5 hour, stay constant. The solid polymer electrolyte consisting of hyper-branched graft polymer was designed to the formation of conductive phase by the phase separation. The electrical conductivity was made by ionic conduction and oxidation-reduction process of iodide supporting electrolyte. In solid polymer electrolyte, the ionic conductivity indicates low because of the restriction of the ion migration. It is assumed that the increase of photocurrent was caused by the optimization of ionic arrangement on the solid polymer electrolyte for the conductivity due to the redox process.

3.3 Electrodeposition of ZnO/N3/polymer electrolyte

The semiconductor thin layer consisting of ZnO can be directly crystallized from aqueous Zn(NO$_3$)$_2$ solution at high temperature by the cathodic electrodeposition as[9]

$$Zn^{2+} + NO_3^- + 2e^- \rightarrow ZnO + NO_2^-$$
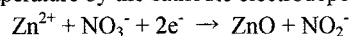
By the cathodic electrolysis at -1.0V (vs. Ag/AgCl) in a solution containing 2 wt% polymer electrolyte, 100 μ mol dm^{-3} N3 and 0.5 mol dm^{-3} Zn(NO$_3$)$_2$, the brown colored thin film was deposited. The thin film deposited with

Table 1   Photoelectrical properties of solar cells using ZnO/N3 deposited electrode with and without polyelectrolyte, exposed to halogen lamp intensity of 110 mW cm^{-2}.

Electrode	Heating time / hour	V$_{oc}$ / V	I$_{sc}$ / μ A cm^{-2}	P$_{max}$ / μ W cm^{-2}	ff	η / %
deposite with SPE	3	0.584	10.4	3.22	0.60	2.93 × 10^{-3}
	24	0.620	10.8	4.16	0.65	3.78 × 10^{-3}
deposite without SPE	3	0.573	6.8	1.76	0.39	1.60 × 10^{-3}
	24	0.615	7.6	1.82	0.452	1.65 × 10^{-3}

polyelectrolyte may be incorporated polymer electrolyte in the ZnO nanoporous films, because of the comparison to color with that without polyelectrolyte.

The values for the photoelectrical properties of solar cells using ZnO/N3 deposited electrode with and without polyelectrolyte are listed in Table 1. In these results, the solar cells using the ZnO/N3 electrode deposited in the presence of polyelectrolyte indicates high performance. It is consider that the composition surface area is improved by the incorporation of polymer electrolyte into ZnO thin film with N3 dye. In the fabrication of solar cells, the photoelectrode deposited with polyelectrolyte not require the separator and additional casting of polyelectrolyte. It is consider that the adherent polymer electrolyte with electrodeposition acts as a separator.

Further, on the photoelectrode by the electrodeposition method, the heating treatment is effectual. Thus, the heating process on the photoelectrode may contribute to the optimization of ionic arrangement on the solid polymer electrolyte for the conductivity due to the redox charge transfer. For the improvement of solar cell performance, the structure of hyper-branched graft copolymer and composition of the redox electrolyte require improvement.

4. CONCLUSION

The solid polymer electrolyte consisting of the hyper-branched graft copolymer can be used for the polyelectrolyte of the true-solid dye-sensitive solar cell. These results indicate that the hyper-branched graft copolymer has potential to be applied to a solid polymer electrolyte using the redox charge-transfer supporting electrolyte. Further, the adherent polymer electrolyte in the electrodeposition of ZnO thin film acts as electrode separator. Thus, for the simplification of fabrication process of dye-sensitized solar cells, the polymer electrolyte is useful in conjunction with the electrodeposition of photoelectrode.

4. REFERENCES

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