

Development of Dye-sensitized Solar Cell Using Solid Polymer Electrolyte Consisting of Hyper-branched Graft Polymer

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Solid-state dye-sensitized solar cells were fabricated with solid polymer electrolyte consisting of I/I_3^- redox couple supporting electrolyte and a hyper-branched graft copolymers of poly(methyl methacrylate-co-chloromethylstyrene)-g-poly[(oxy-ethylene)₉ methacrylate] (PMMA-g-POEM₉) synthesized by atom transfer radical polymerization (ATRP). The photoelectrochemical performances shows the low efficiency for energy conversion, in comparison to the cells with liquid electrolytes, due 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 use of polyethyleneglycole (PEG) solution and heating treatments of solar cells were examined. On the Dye-sensitized solar cells (DSSCs) improved these methods, the short circuit current density and the open circuit voltage obtained for an incident light intensity of 110 mW cm⁻² were uplifted to 0.571 mA cm⁻² and 0.599 V, respectively. This corresponds to an overall efficiency to electric energy conversion efficiency and fill factor of 0.228 % and 0.734, respectively.

Key Words: dye-sensitized solar cell, solid polymer electrolyte, hyper-branched graft polymer, heat treatment

1. INTRODUCTION

DSSCs have been attracting much attention, since O'Regan and Grätzel reported especially high conversion efficiency approaching 10%.¹⁻³ Because a DSSC has attractive properties, low cost, ease of fabrication, high light-to-electricity conversion efficiency compared to inorganic solar cells. Recently, energy conversion efficiency of liquid-electrolyte-based DSSC has been archived to more than 11%.⁴ Even now, there have been various attempts to improve the cell performance. An electrolyte usually used in the cells is an I/I_3^- redox couple in a mixture of ethylene carbonate and propylene carbonate. In DSSCs using liquid electrolytes, major problems are difficulty in sealing, leakage of liquid electrolytes and less long-term stability. Solid or polymer electrolytes have been developed to avoid the leakage and evaporation of the organic solvents. The solid-state dye-sensitized solar cell with polymer electrolyte based on poly(epichlorohydrin-co-ethylene oxide) has been assembled by Paoli.⁵ However the overall energy conversion efficiency of the DSSCs was only 0.22%. This may be related to the low conductivity of the electrolyte and the imperfect contact between the polymer electrolyte and nanocrystalline TiO₂ film electrode.

In the previous study,⁶ hyper-branched graft copolymer was synthesized by atom transfer radical polymerization (ATRP). The polymer is consisting of

covalently-bonded two chemically different polymer segments. One of the polymer segments has high glass transition temperature (T_g) and the other segment has low T_g and high solubility of supporting electrolyte. Thus, the branched polymer has the properties of both high mechanical strength and high electric conductivity. A macroinitiator of poly(MMA-co-CMS) for ATRP is prepared by copolymerization of methyl methacrylate (MMA) and chloromethylstyrene (CMS). A hyper-branched graft copolymer of PMMA-g-POEM_x is synthesized by grafting POEM_x side chains on the macroinitiator using ATRP, that can be obtain a graft polymer having a narrow distribution of a polymerizing degree.

In this study, the solid-state DSSCs, 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. Furthermore, the improvement of performance caused by the low conductivity of polymer electrolyte and the imperfect contact between polymer electrolyte and nanocrystalline semiconductor film electrode was considered.

2. EXPERIMENTAL

2.1 Preparation of hyper-branched graft polymer

A macroinitiator of poly(MMA-co-CMS) for ATRP was prepared by copolymerization of methyl

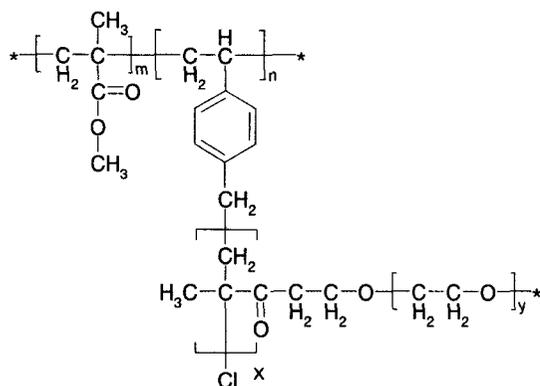


Fig.1 Chemical structure of the hyper-branched graft copolymer poly(MMA-g-POEM_x).

methacrylate (MMA, Aldrich chemicals Co. Inc., USA) and chloromethylstyrene (CMS, Aldrich chemicals Co. Inc., USA) by a conventional radical polymerization in *n*-methylpyrrolidinone (NMP, Aldrich chemicals Co. Inc., USA) solution with 2,2'-Azobisisobutyronitrile (AIBN, Wako pure chemical industry Co. Ltd., Japan) as an initiator. MMA/CMS composition was measured by nuclear magnetic resonance spectra using spectrometer for ¹H (JNM-EX270 FT NMR system, JEOL Ltd., Japan). The hyper-branched graft copolymer was synthesized using ATRP by grafting Poly(ethylene glycol) methyl ether methacrylate (POEM₉, Aldrich chemicals Co. Inc., USA) side chains on the macro-initiator. This reaction was carried out in NMP solution with Copper chloride (Kanto Chem. Co. Inc., Japan) and 4,4'-dimethyl-2,2'-dipyridyl (bpy, Aldrich chemicals Co. Inc., USA). The chemical structure of the hyper-branched graft copolymer is shown in Fig.1. The preparation of hyper-branched grafting copolymer was carried out in a manner similar to the previous paper.⁶

The thermogravimetry analysis were carried out on JEOL 220 TG/DTA system (JEOL Ltd., Japan) under a nitrogen atmosphere. The differential scanning calorimetry were performed with SSC 5220 (Seiko Instruments, Japan) with heating rate at 10 K min⁻¹ and cooling rate at 5 K min⁻¹ in the temperature range from -100 to 200°C.

2.3 Preparation of TiO₂ dye-sensitized electrodes

Nanocrystalline TiO₂ films were prepared by spreading a viscous dispersion of TiO₂ powder (AMT-100; TiO₂ crystal size; 6nm, Tayca Corp., Japan) with water and ethyl alcohol mixture solution on a conduction glass support (Asahi FTO glass, fluorine-doped SnO₂ overlayer, transmission >85% in the visible sheet resistance 10 Ω /square) with heating for 30min at 450 °C. Nanocrystalline TiO₂ films (20 μm 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-dye solution in *tert*-butylalcohol. The N3-dye was purchased from Kojima Chemicals Co., Ltd. (Japan).

2.4 Preparation of dye-sensitized solar cells

Onto the dye-sensitized electrode, the acetone solution containing 25% polyethyleneglycole (PEG, M_w=300), 2.5% LiI, 2.5% I₂, 5% *tert*-butylpyridine (TBP) was cast. These reagents were purchased from Wako pure chemical industry Co. Ltd. (Japan). The dye-coated TiO₂ electrode was covered with the solid polymer electrolyte layer by casting method using an acetone solution containing of 2% (w/w) poly(MMA-g-POEM_x) graft copolymer, 0.1 mol dm⁻³ I₂ and 0.01 mol dm⁻³ LiI. After that, the electrode was drying at 90°C for 24 hour. The modified TiO₂ electrode was incorporated into thin-layer sandwich-type cell with Pt black coated ITO electrode as the counter electrode, spacer film, and electrolyte to measure the solar cell performance.

2.4 Electrochemical measurements

The ionic conductivity of the solid polymer electrolyte was determined with an alternating current impedance technique on 3532-80 (HIOKI E. E. Corp., Japan) impedance analyzer at 25 °C. The solid polymer electrolyte was melted before a "aluminum / electrolyte / aluminum" type cell was assembled.

The photovoltage and photocurrent were measured with the potentiogalvanostat HA-303 (Hokuto Denko Co., Ltd., Japan), function generator HB-104 (Hokuto Denko Co., Ltd., Japan) and X-Y recorder F-35A (Riken Denshi Co., Ltd., Japan). The light source was halogen lamp (100V, 300W) focused to 110 mW cm⁻². Intensity of the incident light was checked with high sensitivity spectro multichannel photodetector MCPD-7000 (Otsuka Electronics Co., Ltd., Japan), by placing the probe 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 Characterization of hyper-branched graft copolymer

The characterization of the hyper-branched graft copolymer, PMMA-g-POEM₉, was measured. The composition of CMS in the macroinitiator was calculated from the 1H NMR spectra. The ratio of MMA and CMS in main chain are 98.6 mol% and 1.4 mol%, respectively. The contents of POEM₉ were 51% (w/w).

The PMMA-g-POEM₉ graft copolymer after vacuum drying was characterized thermogravimetrically. The weight was remarkably decreased beyond 270°C. Thus, the thermal decomposition of the graft polymer is considered to occur beyond 270°C.

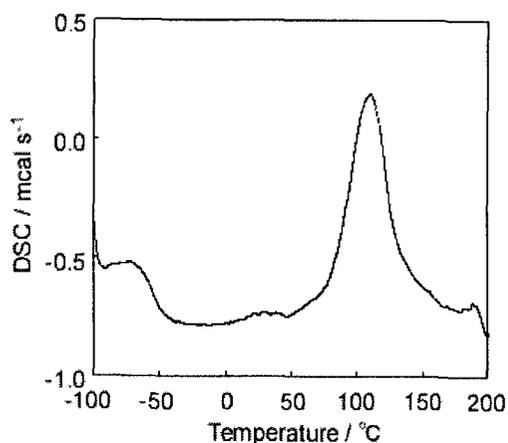


Fig.2 The result of differential scanning calorimetry on the hyper-branched graft polymer, PMMA-g-POEM₉. Sample weight, 10.0 mg; temperature range, -100-200°C; heating rate, 10 K min⁻¹.

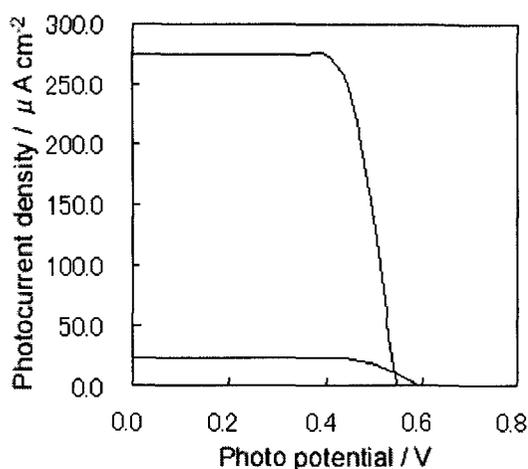


Fig.3 Current-voltage curves of the DSSCs fabricated with solid polymer electrolyte containing 0.1 mol dm⁻³ I₂ and 0.1 mol dm⁻³ LiI with (a) and without (b) PEG/I₂/LiI/TBP solutions.

Fig. 2 shows the DSC profiles of PMMA-g-POEM₉. In this results, a clear exothermic peak was observed at temperatures of 80 to 150 °C was observed. It is assumed that the crystallization of MMA chain, conduced to a higher mechanical strength, was occurred. The crystallization of MMA chain may lead to the phase separation of conductive phase consisting of POEM₉ graft chain conduced to a higher ionic conductivity.

3.2 Conjugation solid polymer electrolyte to nanocrystalline TiO₂ film electrode

In generally, the various battery cells using the solid polymer electrolyte indicates low power outputs. A part of a reason is the lower composition surface area between solid polymer and surface of electrode, because of the

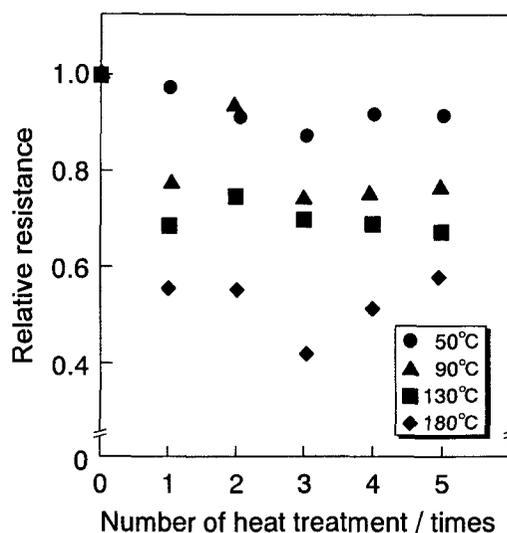


Fig.4 Relationships between number of times of heat treatment at various temperature (15min) and relative resistance of solid polymer electrolyte consisting of PMMA-g-POEM₉, 0.1 mol dm⁻³ I₂ and 0.1 mol dm⁻³ LiI.

viscosity of a solid polymer electrolyte and/or a solid polymer solution. Fig. 3 shows the photocurrent-voltage curve of a DSSC fabricated with the solid polymer electrolyte. It exhibits a short circuit photocurrent (I_{sc}), an open circuit photovoltage (V_{oc}), and a fill factor (ff) of 0.0226 mA cm⁻², 0.596 V and 0.738, respectively. The electric energy conversion efficiency (η) corresponding to an overall light was $9.03 \times 10^{-3} \%$. The fill factor (ff) of the dye-sensitized solar cells can be calculated from the equation,

$$ff = P_{max} / (I_{sc} \times V_{oc}) \quad (1)$$

where P_{max} is the maximum electrical power obtained. The overall internal light to electricity conversion efficiency is obtained by the following relationship,

$$\eta = \frac{P_{max}}{I_s A T} = \frac{I_{sc} V_{oc} ff}{I_s T A} \quad (2)$$

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.

For the improvements of the conjugation, the sandwich-cell was fabricated with solid polymer electrolyte and PEG/I₂/LiI/TBP solution. In this result, the photocurrent of a DSSC improved up to 0.275 mA cm⁻² by the precasting of PEG solution. In addition, ff and η become 0.733 and 0.101%, respectively. It means that the PEG/I₂/LiI/TBP solution was introduced into deep part of nanocrystalline TiO₂ films and works as bridge between surface of nanocrystalline TiO₂ and solid polymer electrolyte. For that reason, with the increase of the effective surface area of dye-sensitized electrode,

Table I Photoelectrical properties of solar cells fabricated with solid polymer electrolyte using PMMA-g-POEM, treated by various heat conditions, exposed to halogen lamp intensity of 110 mW cm⁻².

Conditons	V _{oc} / V	I _{sc} /mA cm ⁻²	P _{max} /mW cm ⁻²	ff	η / %
Non-treatment	0.547	0.275	0.111	0.733	0.101
180°C	0.547	0.311	0.140	0.823	0.128
150°C	0.586	0.494	0.222	0.786	0.202
130°C	0.612	0.460	0.230	0.817	0.209
120°C	0.599	0.571	0.251	0.734	0.228

the performance of a DSSC is elevated.

3.3 Improvement of solid polymer electrolyte by the heat treatments

The influence of heat treatments on the conductivities of solid polymer electrolyte was examined. Fig.4 shows the changes of conductivities of solid polymer electrolytes heat-treated for 15min. at various temperature in many batches. The ionic conductivity increases with increasing temperature and a number of times of heat treatment. It means that the crystallization of main chain caused by the heat treatments leads to promote formation of conductive phase. The optimization of ionic arrangement on the solid polymer electrolyte was occurred. 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 conducting phase. Thus, the heat treatments promote the formation of conducting phase by the crystallization of the MMA chain.

The influence of heat treatment on DSSCs fabricated with solid polymer electrolytes was examined. The comparison of their photocurrent-voltage characteristics is shown in Table I. The cell output performance is improved by the heat treatments. It means that the heat treatment led to the increase of the ionic conductivity due to the optimization of phase transition of hyper-branched graft polymer in electrolyte. But, the current-voltage performance of DSSCs treated at higher temperature, indicates lower values. Perhaps there is something wrong component on the conductivity in heat treatments at high temperature, such as swelling of graft polymer with PEG solution.

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. Furthermore, the problems of DSSCs using solid polymer electrolytes, such as the lower effective surface area of conjugation between nanocrystalline TiO₂ electrode and

polymer electrolyte, and low conductivity of polymer electrolyte, can be improved by using PEG/I₂/LiI/TBP solution and periodic heat treatments. However, heat treatments under higher temperature cause lowering of photocurrent-voltage performance of DSSCs. Thus, these treatments can be improved for these problems, but the development of more suitable improved process is needed.

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