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Highly efficient quasi-solid state dye-sensitized solar cell with ion conducting polymer electrolyte

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Abstract

Quasi-solid state dye-sensitized solar cells were fabricated using an oligomer having three polymerizable reactive groups. Only 7% polymer concentration in the polymer electrolyte is found enough to form a stable quasi-solid structure and a three-dimensional polymer network structure is proposed. Conductivity measurement of the polymer electrolyte in different organic solvents shows that the ionic conductivity increases with decreasing the viscosity of the solvent and a high ionic conductivity of 9 mS/cm is observed for the polymer electrolyte composition of 0.2 M DMPII, 0.5 M LiI, 0.05 M I_2 in the mixed solvent of ethylene carbonate and γ-butyrolactone (30:70 v/v). A short circuit photocurrent density of 14.8 mA/cm^2, an open circuit voltage of 0.78 V, a fill factor of 0.70 and an overall conversion efficiency of 8.1% under AM1.5 irradiation (100 mW/cm^2) was observed when fabricated a quasi-solid state dye-sensitized solar cells using these high conducting polymer electrolyte. The quasi-solid cells with the polymer electrolyte show higher open circuit voltage than that of the liquid cells that may be due to the suppression of the back electron transfer between the conduction band of the TiO_2 electrode and the triiodide ion in the electrolyte.

Keywords: Dye-sensitized solar cell; Quasi-solidification; Polymer electrolyte; Three-dimensional network; Ionic conductivity

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1. Introduction

Recently dye-sensitized solar cells (DSC) have been widely investigated as a new type of solar cell because of its simple structure, easy production, and higher energy conversion efficiency (10%) [1,2]. In general, DSC comprises an electrode consisting of a nanocrystalline titanium dioxide (TiO_2) films modified with a dye, a platinum counter electrode and an electrolyte solution in between the electrodes. Photoexcitation of the dye results in the injection of an electron into the conduction band of the oxide. The original state of the dye is subsequently restored by electron donation from a redox system, such as the iodide/triiodide couple. At the present DSC is mainly constructed by using liquid electrolyte as a charge transport material. The charge transport in these liquid electrolytes is typically achieved by using an iodide/triiodide ($I^-/I_3{}^-$) redox reaction in electrolyte solution. Therefore, long-term durability of DSC is limited by leakage of liquid electrolyte. In order to solve this problem, several papers have been reported the studies of organic and inorganic p-type semiconductors as a solid-state charge transport materials [3]. However, the efficiency of these solid-state cells was unsatisfactory compared to that using the liquid electrolyte due to low charge transport ability of the p-type semiconductors and poor contact of the solid-state charge transport material with the dye coated TiO_2 surface.

An alternative approach to solid-state charge transport materials is the use of quasi-solid state charge transport materials, such as molten salt [4] and polymer electrolyte [5,6]. Polymer electrolytes have as high ionic conductivities as liquid electrolyte and also suppress the solvent leakage. Yanagida and coworkers have developed quasi-solid state DSC with polymer electrolyte formed by oligomer structure with one or two polymerizable group [5]. The energy conversion efficiency of quasi-solid state DSC was reported to be 2.62%. This efficiency is much lower than that of liquid DSC reported by Grätzel et al. In order to increase the conversion efficiency of quasi-solid state DSC, the polymer network needs to be formed by chemical bond and to be able to keep large amount of liquid electrolyte. Therefore, we have used poly(ethylene oxide-co-propylene oxide) trimethacrylate (oligomer) having three polymerizable reactive groups (Fig. 1). By crosslinking reactions among the reactive groups of this oligomer, it is considered that a three-dimensional

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network polymer is formed [7] where the oligomers are connected through chemical bond. In this study, we report the quasi-solidification of DSC with ion conducting polymer electrolyte which is formed by three-dimensional network polymer.

2. Experimental

2.1. General procedure for cell preparation

Porous TiO_2 electrode of about 10 μm thick on F-doped SnO_2 conducting glass was prepared using a published procedure [8]. The area of prepared porous TiO_2 electrode was $25\,mm^2$ (5 mm × 5 mm). Dye absorption was carried out by dipping TiO_2 electrode in a 4×10^{-4} M ethanolic solution of Ru (2,2′-bipyridine-4,4′-dicarboxylic acid)$_2$ (NCS)$_2$. Oligomer **1** (1.0–5.0 g) (Fig. 1), polymerization initiator (AIBN: azobisisobutyronitrile, 4 wt.% of weight of oligomer) and organic solvent (20 g) were mixed at room temperature. Propylene carbonate [PC], ethylene carbonate [EC], butylene carbonate [BC], γ-butyrolactone [GBL] and a mixture of these solvents were used as organic solvent. The oligomer solution was introduced to the dye coated TiO_2 electrode and covered by a slide glass using polyimide spacer (25 μm) in between electrode and slide glass (Scheme 1). The electrode was heated at 363 K for 1.5 h to complete polymerization. After quasi-solidification of the solution, slide glass was removed and the electrode was immersed in an electrolyte solution containing, 0.05 M I_2, 0.5 M LiI and x M 1,2-dimethyl-3-propyl imidazolium iodide (DMPII, $x = 0$, 0.2, 0.3 and 0.5) in an organic solvent same as used in the oligomer solution for 1 h to permeate redox species into the polymer network. Then a platinum coated counter electrode was attached to the polymer electrolyte to prepare a two-electrode sandwich cell for photo-electrochemical measurements.

2.2. Measurement

Commercially available stainless-steel electrode cells were used for the conductivity measurements. The conductivity of polymer electrolyte prepared in the cell (8 mm diameter, 0.5 mm thick) was measured at 298 K by means of the complex impedance measurement by frequency response analyzer (Hewlett-Packard 4192A LF impedance analyzer) in the frequency range 10 Hz to 250 kHz (signal amplitude 5 mV). Viscosity of solvent was measured at 298 K with E-type viscometer (Tokyo-Keiki, Visconic ED type). Photoelectrochemical properties of prepared DSC were measured with solar simulator (AM1.5, $100\,mW/cm^2$, WXS-155S-10: Wacom Denso Co., Japan) as a light source, and computer-controlled digital source meter (Keithley, Model 2400).

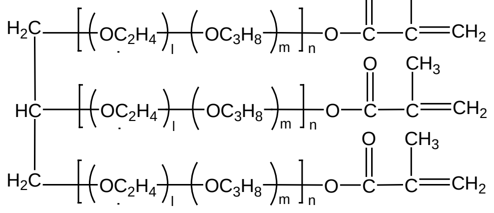
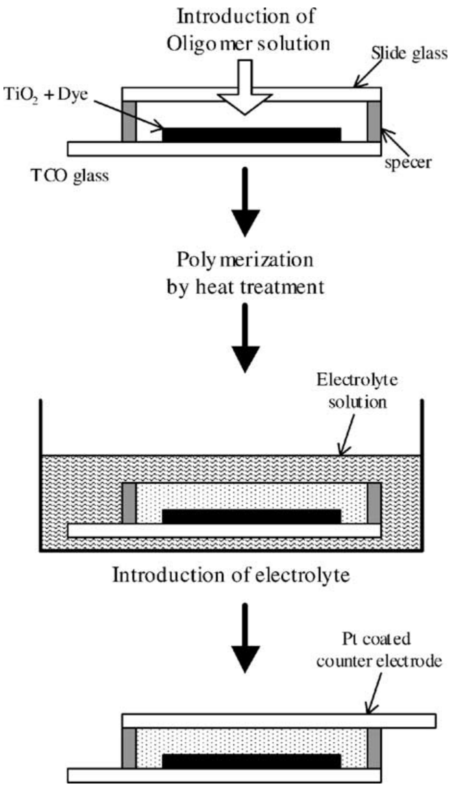


Fig. 1. Structure of oligomer used in this study.



Scheme 1. Preparation scheme of quasi-solid cell.

3. Results and discussion

Fig. 2 shows the dependence of the ionic conductivity at 298 K on the polymer concentration in the polymer

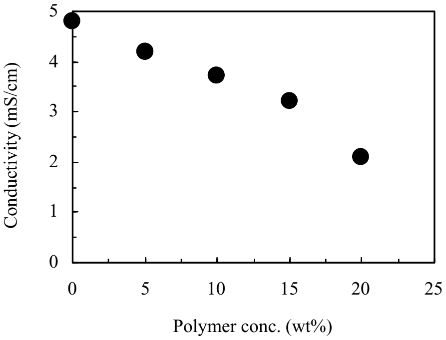


Fig. 2. Dependence of the conductivity on the polymer concentration in the polymer electrolyte. Electrolyte composition was 0.5 M LiI and 0.05 M I_2 and using organic solvent is PC.

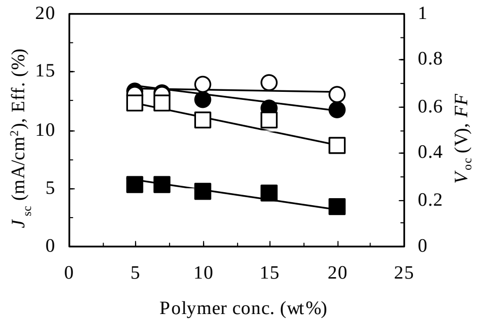


Fig. 3. Polymer concentration dependence of cell properties (filled circle: J_{sc}; open circle: V_{oc}; filled square: eff.; open square: FF; electrolyte composition was 0.5 M LiI and 0.05 M I_2 and using organic solvent is PC. TiO_2 thickness was 10 μm).

electrolyte. It is found that the ionic conductivity increases with decreasing polymer concentration, which suggests that polymer in the electrolyte hinders ionic movement. However, using the oligomer **1** with three polymerizable reactive groups, a quasi-solid state form can be kept until the polymer concentration decrease to 5% and the conductivity at polymer concentration of 5% ($\sigma = 4.2 \times 10^{-3}$) is close to that of liquid electrolyte ($\sigma = 4.8 \times 10^{-3}$). To prepare a quasi-solid form of polymer electrolyte using an oligomer with one or two polymerizable reactive groups, a large amount of polymer concentration (20%) was needed [3]. This result showed that polymer electrolyte using the oligomer **1** with three polymerizable groups could keep a large amount of liquid electrolyte because of its large free volume. It was considered that using this oligomer a three-dimensional network structure had been formed. Therefore, this result implies that high cell performance could be expected by using this polymer electrolyte.

Fig. 3 shows the dependence of the cell properties on the polymer concentration in the polymer electrolyte. Electrolyte composition was 0.5 M LiI and 0.05 M I_2 and using organic solvent is PC. It is found that energy conversion efficiency (eff.) increases proportional to decrease of polymer concentration because short circuit photocurrent density (J_{sc}) and fill factor (FF) increase, while open circuit voltage (V_{oc}) keeps nearly constant. Both J_{sc} and FF are influenced by the ionic conductivity of polymer electrolyte, because low conductivity causes rate-determining of charge transportation and increasing the series resistance, while V_{oc}, a difference between Fermi level of TiO_2 and redox potential of electrolyte, is influenced mainly by the molar ratio of I^-/I_3^-. In this case, I^-/I_3^- molar ratio is independent of the polymer concentration and thus V_{oc} shows a constant value.

During the cell preparation the quasi-solidification of the electrolyte was occasionally failed below the polymer concentration of 5%, because of its fragility. However, polymer electrolyte with polymer concentration of above 7% was stable polymer electrolyte. Therefore, polymer concentration of 7% was chosen in the following experiments.

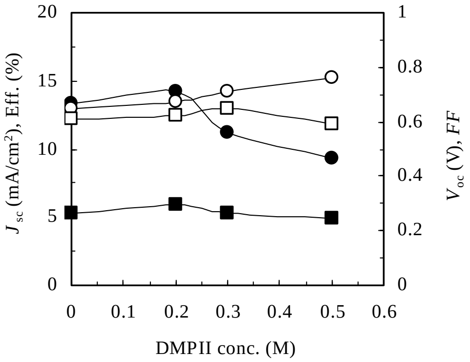


Fig. 4. DMPII concentration dependence of cell properties (filled circle: J_{sc}; open circle: V_{oc}; filled square: eff.; open square: FF; electrolyte composition was x M DMPII, 0.5 M LiI, 0.05 M I_2 and using organic solvent is PC. Polymer concentration was 7 wt.% and TiO_2 thickness was 10 μm).

Furthermore, 1,2-dimethyl-3-propyl imidazolium iodide (DMPII) is usually used to increase the cell efficiency in the case of liquid cell. DMPII was also added to the polymer electrolyte to increase efficiency. Fig. 4 shows the dependence of cell properties on DMPII concentration. It is found that V_{oc} increases with the increase of DMPII concentration. The increase of V_{oc} can be explained as follows. According to Nernst equation, increasing the concentration of reduction species causes shifting the redox potential to more negative value. The redox potential (E) can be expressed by Nernst equation [9]:

$$E = E^0 - \frac{RT}{nF} \ln\left(\frac{a_R}{a_o}\right) \tag{1}$$

Here E^0 is the standard electrode potential, R the gas constant, T the absolute temperature, n the electron number per one reaction species, F the Faraday constant, a_R the activity of reduction species and a_o is the activity of oxidation species.

In the case of DSC, the reduction species is I^- and the concentration of I^- in the polymer electrolyte increases when DMPII is added. From Eq. (1) the redox potential of iodide/triiodide (I^-/I_3^-) is shifted to more negative value by the addition of DMPII. Then V_{oc} should decrease because the energy gap between the Fermi level of TiO_2 and the redox potential of I^-/I_3^- becomes smaller. However, V_{oc} increased with adding DMPII. It was considered that increase of V_{oc} had been caused by increase of DMPI cation from DMPII. In general, adding 4-*tert*-butylpyridine (TBP) causes increase of V_{oc} [2]. It has been considered that TBP is adsorbed at the TiO_2 surface and suppress the back electron transfer from TiO_2 to the I_3^- and then a high value of V_{oc} is observed. Adsorption of TBP at TiO_2 surface is caused by interaction between Ti(IV) ion that has Lewis acidity and lone electron pair of TBP. DMPI cation also has lone electron pair. Presumably DMPI cation adsorbs at TiO_2 surface by interaction between Ti(IV) ion and lone electron pair of DMPI cation.

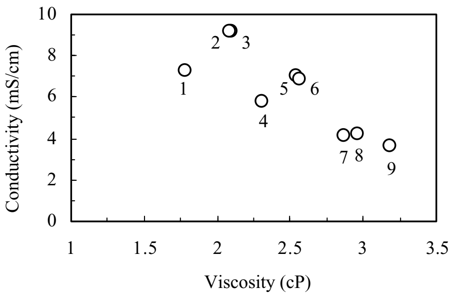


Fig. 5. Solvent viscosity dependence of conductivity (polymer electrolyte) at 298 K. Electrolyte composition was 0.2 M DMPII, 0.5 M LiI, 0.05 M I_2. Polymer concentration was 7 wt.% (1: GBL; 2: PC/GBL; 3: EC/GBL; 4: BC/GBL; 5: PC; 6: EC/PC; 7: PC/BC; 8: EC/BC; 9: BC; mixing ratio was 50:50 v/v).

In the various DMPII concentration the maximum J_{sc} showed at the DMPII concentration of 0.2 M. For efficient charge transportation in the polymer electrolyte, ionic concentration ratio of I^-/I_3^- is important because charge transportation in electrolyte of DSC carried out by redox reaction of I^-/I_3^-. Therefore, it is considered that ionic concentration ratio for charge transportation is optimized at the DMPII concentration of 0.2 M. The maximum efficiency of 6.0% was obtained at the electrolyte composition of 0.2 M DMPII, 0.5 M LiI, 0.05 M I_2.

To improve the ionic conductivity of the polymer electrolyte, a number of organic solvents were investigated. PC, EC, BC, GBL and a mixture of these solvents were used, and viscosity of those solvents was measured before mixing with the oligomer. Fig. 5 shows the dependence of the ionic conductivity of polymer electrolyte on the viscosity of corresponding solvents. The ionic conductivity increases with decrease of viscosity. However, a high ionic conductivity of about 9 mS/cm was obtained at a low viscosity of 2.1 cP with mixed solvent of EC/GBL (Fig. 5). It is well known that GBL is a low viscosity solvent and EC is a high viscosity solvent. Generally ionic conductivity (σ) is determined by [10]

$$\sigma = F|z|\mu c \tag{2}$$

Here F is the Faraday constant, z the ionic charge number, c the ionic concentration and μ is the ionic mobility. In Eq. (2), F is constant. The value of z is assumed to be constant because it is considered that absolute charge number of all charge carriers (I^-, I_3^-, Li^+ and DMPI cation) in the electrolyte is 1. Therefore, σ is varied with change of the ionic concentration and the ionic mobility. The effective ionic concentration increases when the solvent with high dielectric constant was used, because iodide compound can be easily dissociated in this solvent. On the other hand, the ionic mobility is influenced by viscosity of solvent and ion can move easily in the solvent with lower viscosity. Since EC shows high dielectric constant and GBL shows low viscosity, a high value of ionic conductivity is expected with the mixed solvent of EC/GBL.

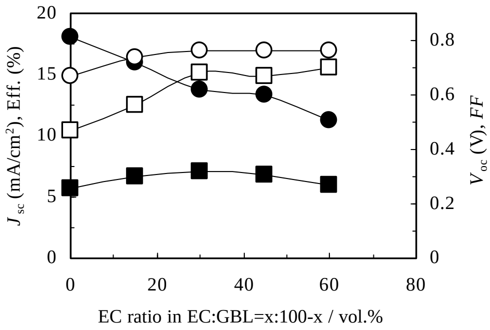


Fig. 6. EC/GBL ratio dependence of photocurrent–voltage properties (filled circle: J_{sc}; open circle: V_{oc}; filled square: eff.; open square: FF) electrolyte composition was 0.2 M DMPII, 0.5 M LiI, 0.05 M I_2 and polymer concentration was 7 wt.%. TiO_2 thickness was 10 μm.

Furthermore, the dependence of the cell properties on the mixing ratio of EC and GBL was investigated, as shown in Fig. 6. It is found that J_{sc} decreases with increase of EC concentration in EC/GBL mixed solvent. Following two reasons are considered to explain the decreases of J_{sc}. One is the decrease of ionic conductivity because of increasing the solvent viscosity with increasing EC content (from Eq. (2)). The other is that the TiO_2 porous electrode is hardly filled with polymer electrolyte because the oligomer with high viscosity solvent is difficult to permeate into the TiO_2 porous electrode. Both V_{oc} and FF increases with increasing EC content and reaches a constant value over 30 vol.% of EC. A high conversion efficiency of 7.0% was obtained with 30 vol.% of EC and 70 vol.% of GBL.

A thickness of 10 μm TiO_2 porous electrode was used in the above study, because the thickness of 10 μm was optimized in the condition of the polymer electrolyte with PC. However, it is considered that the EC/GBL mixed solution could be permeated into the thicker TiO_2 porous electrode than that of PC, because viscosity of EC/GBL solvent is lower than that of PC solvent. Therefore, it is considered that J_{sc} increases with the thicker TiO_2 porous electrode, because of increasing the amount of absorbed dye. Fig. 7 shows photocurrent–voltage curves using two different thickness (10 and 12 μm) of TiO_2 porous electrode. J_{sc} increased with increase of the TiO_2 thickness. As a result a short circuit photocurrent density of 14.8 mA/cm^2, an open circuit voltage of 0.78 V, a fill factor of 0.70 and an overall conversion efficiency of 8.1% was obtained.

In this study, it is found that the quasi-solid cells with the polymer electrolyte show higher V_{oc} and lower J_{sc} than that with liquid electrolyte although the electrolyte composition is same in both quasi-solid cell and liquid cell. The characteristics of the liquid and quasi-solid cells using EC/GBL mixed solvent were compared in Fig. 8. It was considered that low J_{sc} value had been caused by hindrance to move ion by polymer network. In the same way it was expected that high V_{oc} value had been affected by polymer network. The oligomer (Fig. 1) used in the polymer electrolyte is hydrophilic in nature and the nanocrystalline TiO_2 is also

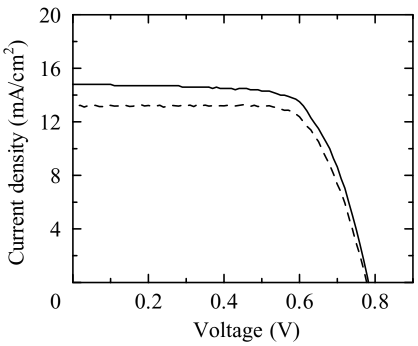


Fig. 7. Photocurrent–voltage characteristics of quasi-solid cells using TiO_2 electrodes of different thickness (broken line: TiO_2 thickness 10 μm; eff. = 7.5%; $J_{sc} = 13.2\,mA/cm^2$; $V_{oc} = 0.78\,V$; FF = 0.73. Solid line: TiO_2 thickness 12 μm; eff. = 8.1%; $J_{sc} = 14.8\,mA/cm^2$; $V_{oc} = 0.78\,V$; FF = 0.70). Electrolyte composition was 0.2 M DMPII, 0.5 M LiI, 0.05 M I_2 and using organic solvent was EC/GBL (30:70 v/v). Polymer concentration was 7 wt.%.

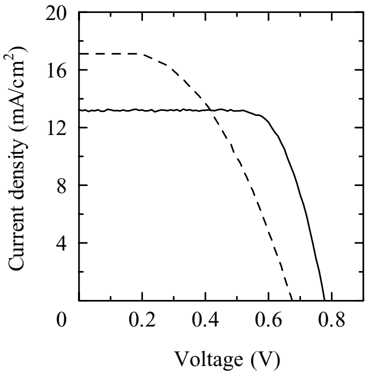


Fig. 8. Photocurrent–voltage characteristics of the liquid (broken line) and quasi-solid (solid line) cells. Electrolyte solution was 0.2 M DMPII, 0.5 M LiI, 0.05 M I_2 and using organic solvent was EC/GBL (30:70 v/v). TiO_2 thickness was 10 μm.

hydrophilic material. When the oligomer is injected to the dye-anchored TiO_2, it is assumed that the polyether chain may be adsorbed on to the surface of TiO_2. Decrease of V_{oc} was related by back electron transfer reaction [11]. Back electron transfer reaction is the reduction of I_3^- obtaining an electron from the conduction band of the TiO_2. Increasing of back electron transfer reaction causes decrease of V_{oc}. When polymerization occurs, the polymer formed in the surface of TiO_2 suppresses the back electron transfer from TiO_2 to the I_3^-, as shown in Fig. 9, and then a high value of V_{oc} is observed.

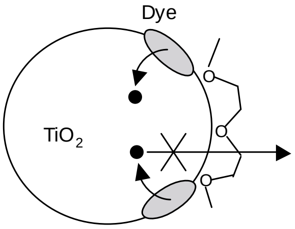


Fig. 9. Proposed mechanism for high value of open circuit voltage in quasi-solid cell.

Although J_{sc} of quasi-solid cells is lower than that of liquid cells, it is considered that it is possible to increase the J_{sc} of quasi-solid cell by optimizing the thickness of TiO_2 electrode. Therefore, it is considered that the efficiency of quasi-solid cell can be further increased.

4. Conclusions

We have succeeded in constructing the quasi-solid state dye-sensitized solar cell with ion conducting polymer electrolyte. Optimization of electrolyte composition, polymer concentration, and thickness of TiO_2 porous electrode are necessary to improve the energy conversion efficiency. An energy conversion efficiency of 8.1% was achieved with ion conducting polymer electrolyte by optimizing the above factors. The cell using the polymer electrolyte shows larger V_{oc} and lower J_{sc} than that using liquid electrolyte. It is expected that the conversion efficiency can improve further by optimizing the thickness of TiO_2 porous electrode and also by improving the composition of the viscosity and dielectric constant of solvent.

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