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Fabrication of Solid-State Dye-Sensitized TiO$_2$ Solar Cell Using Polymer Electrolyte

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A solid-state dye-sensitized TiO$_2$ solar cell has been fabricated with a polymer electrolyte constructed with α-methacryloyl-ω-methoxyocta(oxyethylene) or 2-(2-methoxyethoxy)ethyl acrylate as a base polymer, α-acryloyl-ω-acryloyloxyocta(oxyethylene)octa(ethylene glycol) dimethacrylate as a cross-linking agent and 3-methoxypropiononitrile as a plasticizer. The polymer is *in-situ* polymerized at the porous TiO$_2$ film by photo-irradiation and the resulting film is immersed into the liquid electrolyte in order to introduce the electrolyte to the polymer phase. The conductivity of the polymer electrolyte reached 2.67 mS cm^{-1}. The energy conversion efficiency of the solid-state cell was 2.62% under irradiation of simulated sunlight (AM 1.5, 1 kW m^{-2}), achieving 86.4% of the cell efficiency using the liquid electrolyte.

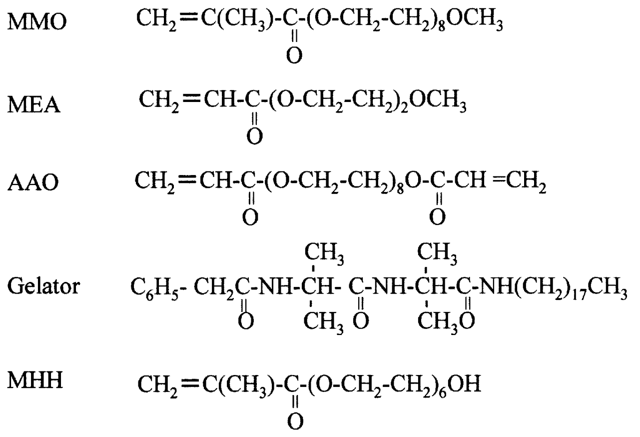
Dye-sensitized TiO$_2$ solar cells have been currently under intense investigation because of their low cost and earth-friendly photovoltaics, with high efficiency comparable to that of silicon solar cells.[1] The major drawback of the module has been recognized to be the use of the liquid electrolyte for hole transport from dye molecules to a counter electrode. The long-term durability of the module was limited due to leakage of the liquid electrolyte containing an organic solvent such as acetonitrile, because of difficulty in sealing it in the module. Replacement of the liquid electrolyte with solid- or quasi-solid-type hole transport materials has been attempted using room temperature molten salt,[2] p-type semiconductors,[3] conducting organic polymers,[4] polymer gel electrolyte,[5] or ionic conductive polymer electrolytes.[6] However, the efficiencies of solid-state cells were found unsatisfactory compared to that using the liquid electrolyte. By using some low molecular weight gelling agents, the authors' group succeeded in constructing a quasi-solid-state cell, achieving the competitive efficiency,[7] but this cell may have a lack of long-term stability under high temperatures because of its relatively low sol-gel transition temperature (40–80 °C).

In our previous reports,[6] poly[α-methacryloyl-ω-hydroxyhexa(oxyethylene)] (PMHH), which is well known as a polymer electrolyte,[8] was applied to constructing a solid-state solar cell. Though high molecular weight polymer should be difficult to intrude into the porous TiO$_2$ film, we adopted a strategy in which the monomer introduced into the pore structure was *in-situ* polymerized. The energy conversion efficiency was still relatively low (40% of cell using the liquid electrolyte) for the cell constructed using this technique due to the following problems. One of the problems was difficulty in controlling the extent of cross-linking of the polymer. In the case of *in-situ* polymerization of α-methacryloyl-ω-hydroxyhexa(oxyethylene) (MHH), it was self-cross-linked by radical transfer to hydroxy group at the end of the side chain. Excess cross-linking should decrease the conductivity of the polymer electrolyte. Secondly, the amounts of iodine introduced into the polymer electrolyte could not be controlled.

In this paper, we succeeded in controlling the extent of cross-linking by using a cross-linking agent, α-acryloyl-ω-acryloyloxyocta(oxyethylene) (AAO) mixed with the monomer α-methacryloyl-ω-methoxyocta(oxyethylene) (MMO) or 2-(2-methoxyethoxy)ethyl acrylate (MEA). We introduced the electrolyte containing iodine and iodide into the polymer matrix by immersing the polymer in the liquid electrolyte so that we could optimize their concentrations in the polymer electrolyte. The obtained polymer electrolyte showed a high conductivity of 2.67 mS cm^{-1}. We applied these polymer electrolytes to constructing a solid-state TiO$_2$ solar cell and achieved the high energy conversion efficiency corresponding to 86.4% of that for the cell using the liquid electrolyte.

Experimental

Materials. All reagents were used as obtained and without further purification. α-methacryloyl-ω-methxyocta(oxyethylene) (PME 400$^{\text{TM}}$: MMO) and α-methacryloyl-ω- hyroxyhexa(oxyethylene) (PE 350$^{\text{TM}}$: MHH) were supplied from Nihon Oil and Fat Co., Ltd. α-acryloyl-ω-acryloyloxyocta(oxyethylene) (PEG 400$^{\text{TM}}$: AAO) and 2-(2-methoxyethoxy)ethyl acrylate (ECA$^{\text{TM}}$: MEA) were supplied from Nippon Kayaku Co., Ltd. (Chart 1). 1-Hydroxy-cyclohxyl-phenyl-ketone (Irgacua® 184) was supplied from Chiba-Geigy. *z*-Val-Val-NHC$_{18}$H$_{37}$ (Gelator) was synthesized as previously reported.[9] A 3-methoxypropiononitrile (MPN)



MMO
$$CH_2{=}C(CH_3)\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}(O\text{-}CH_2\text{-}CH_2)_8OCH_3$$

MEA
$$CH_2{=}CH\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}(O\text{-}CH_2\text{-}CH_2)_2OCH_3$$

AAO
$$CH_2{=}CH\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}(O\text{-}CH_2\text{-}CH_2)_8O\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}CH{=}CH_2$$

Gelator
$$C_6H_5\text{-}\ CH_2\underset{\underset{\displaystyle O}{\|}}{C}\text{-}NH\text{-}\overset{CH_3}{\underset{CH_3}{CH}}\text{-}\ \underset{\underset{\displaystyle O}{\|}}{C}\text{-}NH\text{-}\overset{CH_3}{\underset{CH_3}{CH}}\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}NH(CH_2)_{17}CH_3$$

MHH
$$CH_2{=}C(CH_3)\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}(O\text{-}CH_2\text{-}CH_2)_6OH$$

Chart 1.

solution containing 1,2-dimethyl-3-propylimidazolium iodide (0.6 M; 1 M = 1 mol dm^{-3}: DMPI), iodine (0.1 M) and 4-*t*-butylpyridine (1 M) was used as a liquid electrolyte.[1,7,10]

Preparation of Polymer Electrolytes in the Sandwich Cell for Measuring Their Conductivity. In Fig. 1 are illustrated the structure of the sandwich cell and the procedure of the preparation of the polymer electrolyte for the measurements of conductivity. The cell was constructed with two platinum-coated OTE (Optically Transparent Electrode) glass electrodes and a glass spacer (1 mm thickness) by using adhesive films (HIMILAN 1652, Mitsui-Dupont Polychemical, Japan). The monomer mixture prepared by mixing 70 mg of MMO (as a base polymer), 30 mg of AAO (as a cross-linking agent), 1 mg of Irgacua 184 (as a photo radical initiator) and 100 mg of MPN (as a plasticizer) was introduced into the sandwich cell. The cell was irradiated for 5 min by a solar simulator (AM 1.5, 1000 W m^{-2})[11] to induce polymerization. Then the cell was immersed into the liquid electrolyte for 12 h to permeate the electrolyte into the polymer electrolyte. In order to avoid exfoliation of the electrodes owing to swelling of the polymer by absorbing the solution, the cell was mechanically clamped with two clips. Finally the cell was sealed up with epoxy resin.

Measurements of the Concentrations of I_2 or DMPI in the Polymer. The monomer mixture prepared by mixing MMO (70 mg), AAO (30 mg), Irgacua 184 (1 mg) and MPN (100 mg) was introduced into a quartz-made optical cell (optical length, 1 mm) and irradiated for 5 min by a solar simulator (AM 1.5, 1000 W m^{-2}) to induce polymerization. The optical cell was immersed into an MPN solution of 0.1 M of I_2 or 0.6 M of DMPI so that I_2 or DMPI dissolved in MPN could intrude to the polymer structure through co-diffusion with MPN. Increase of the concentration of I_2 or DMPI in the polymer electrolyte was followed by measuring the absorption at 375 nm and 365 nm for I_2 and DMPI, respectively.

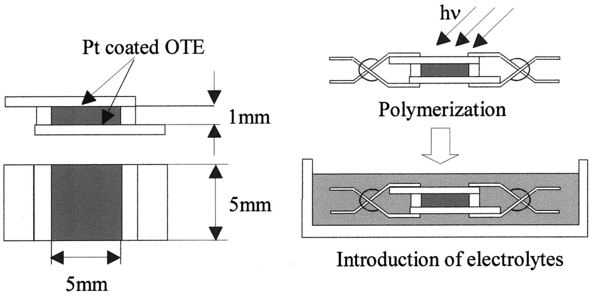


Fig. 1. Structure of the sandwich cell and construction scheme of the polymer electrolyte.

Conductivity of the Polymer Electrolyte. The conductivity of the polymer electrolyte prepared in the cell was measured with an AC impedance analyzing method. The frequency dependence of impedance was measured at 25 °C using a frequency response analyzer (PGZ301: Radiometer, France) on 0.5 V of modulation amplitude.

Solid-State TiO_2 Solar Cells. The dye, *cis*-di(thiocyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4,4′- dicarboxylic acid)ruthenium(II) was synthesized as reported previously.[12] The dye-anchored porous TiO_2 electrode was prepared by using commercially available TiO_2 (P25: Nippon Aerosil Co., Ltd.), and a fluorine-doped SnO_2 layered glass (OTE: sheet resistance of 10 Ω/□, Nippon Sheet Glass Co., Ltd.) as reported previously.[13]

The dye-anchored porous TiO_2 electrode was combined with a platinum-coated OTE glass counter electrode by the adhesive films with a gap of ca. 100 μm. The cell was immersed into the monomer solution under reduced pressure for 5 min so that the solution was introduced into the gap of the cell. Then the cell was irradiated with simulated sunlight for 5 min in order to induce polymerization of the monomer. The cell was immersed into the liquid electrolyte for 12 h and then sealed with epoxy resin.

Photoelectrochemical measurements were performed at 25 °C with a solar simulator (AM 1.5, 1000 W m^{-2}, YSS-80: Yamashita Denso Co. Japan) as a light source, and a computer-controlled digital multimeter for photocurrent (model 166; Keithley, Japan) and voltage (model HP3478A; Hewlett-Packard).[7]

Results and Discussion

Preparation and Characterization of the Polymer Electrolyte. Thermal Durability. Figure 2 show photographs of the obtained polymer piece heated to 50, 100 and 150 °C, respectively. The polymer was hard enough to stand by itself. The shape of the polymer solid did not change even at 100 °C, but showed shrinkage at 150 °C due to evaporation of the plasticizer, MPN. These facts demonstrated that the polymer electrolyte prepared in the present work possesses high durability below 100 °C, which should be appropriate for application to the dye-sensitized solar cell for solidification of the hole transport layer.

Concentration of I_2 or DMPI Introduced into the Polymer Matrix by Immersion. When the optical cell containing the polymer MMO cross-linked with AAO was immersed in an MPN solution containing I_2 or DMPI, the concentration of DMPI in the polymer matrix increased and reached a plateau within 6 h, as shown in Fig. 3. On the other hand, that of iodine increased slower than DMPI, attaining the plateau after 12 h. It was shown that both the concentrations reached to the same concentrations as the immersing liquid electrolyte.[14] The energy conversion efficiency of the dye-sensitized solar cell is affected by the amount and composition of the liquid electrolyte in the hole transport layer. Now we could construct the polymer electrolyte with the optimized composition for the liquid electrolyte as the hole transport layer of the dye-sensitized cell. The same equilibrium potential (–20 mV vs. Ag/Ag^+) of the polymer electrolyte as observed for the liquid electrolyte also

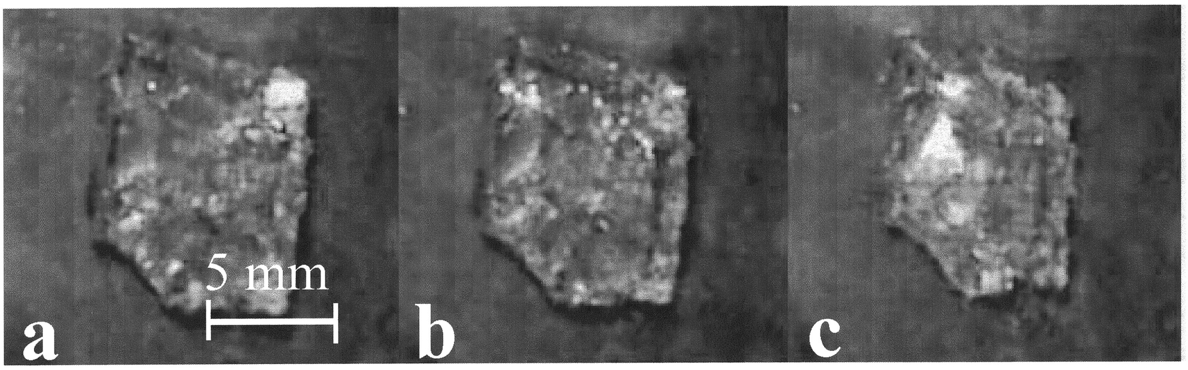


Fig. 2. Photographs of the polymer electrolyte at various temperatures. polymer: MMO/AAO/MPN = 7/3/10, a: 50 °C, b: 100 °C, c: 150 °C.

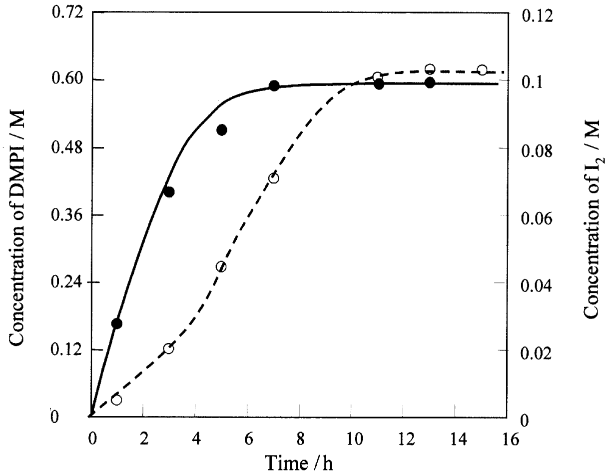


Fig. 3. Changes of the concentrations of DMPI and I_2 in the polymer electrolyte. Polymer: MMO/AAO/MPN = 7/3/10, solid line: DMPI, broken line: I_2.

indicated that the polymer electrolyte has the same electrochemical potential as the liquid electrolyte. In the following experiments we fixed the immersing time of the cell at 12 h.

Effect of Cross-Linking Agent on the Conductivity. The conductivity of the polymer electrolyte depended strongly on the content of the cross-linking agent (Fig. 4). The conductivity increased gradually with decrease of the content; it showed a rapid jump below 50% and reached 1.42 mS cm^{-1} at 20%. The polymer could no longer retain the gel structure at less than 20% of AAO, resulting in the formation of liquid. It is well known that the cross-linking reduces the flexibility of the polymer, resulting in the low conductivity.[15] So, it is important to select a minimum amount of cross-linking agent which is still enough to maintain the desired strength of the gel. The concentrations of the cross-linking agent less than 40% of AAO were employed in the following experiments.

Effect of Plasticizer on the Conductivity. Figure 5 shows dependencies of the conductivity on the content of plasticizer (MPN) in the polymer electrolytes prepared with various compositions of the base-polymer and the cross-linking agent. The conductivity increased with increasing of the content of the plasticizer above 30% and reached 2.6 mS cm^{-1} at 80% of NMP. The increasing behavior of the conductivity with increase of the plasticizer did not show any large differences among the polymer electrolytes prepared from the different compositions of MMO and AAO. Dependence of logarithm of the conductivity on temperatures gave a slightly convex line; such a shape was typical for polymer electrolytes and is known as Williams–Landel–Ferry[16]-type temperature-dependence (data not shown). But the small bending of the curve suggested that the contribution of the polymer to the ionic conductivity was relatively low. These facts indicated that the conductivity was mainly determined by the contents of the plasticizer rather than by the property of the polymer.

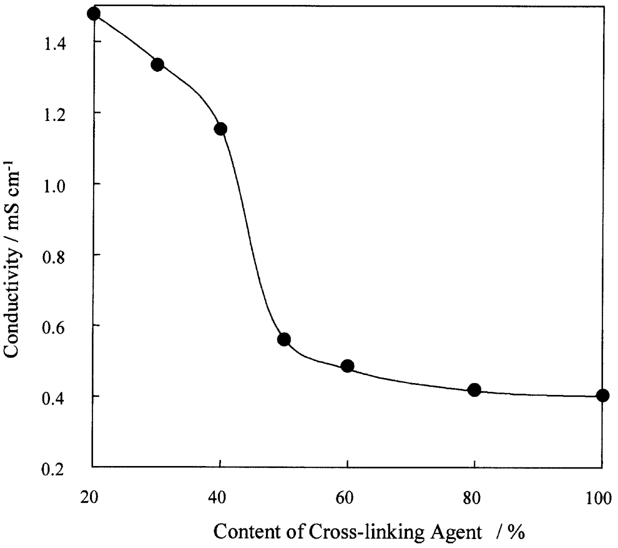


Fig. 4. Dependence of the conductivity on the content of the cross-linking agent. Content of the cross-linking agent: AAO/(MMO + AAO), (wt/wt). Content of the plasticizer: 50% (wt/wt).

The conductivity of the polymer electrolyte of HEM (80% of the plasticizer, 1.6 mS cm^{-1}) was 1.5 times smaller than that of MEA/AAO at the same content of the plasticizer (2.4 mS cm^{-1}) because the cross-linking rate of HEM was not controlled as described in the introduction.

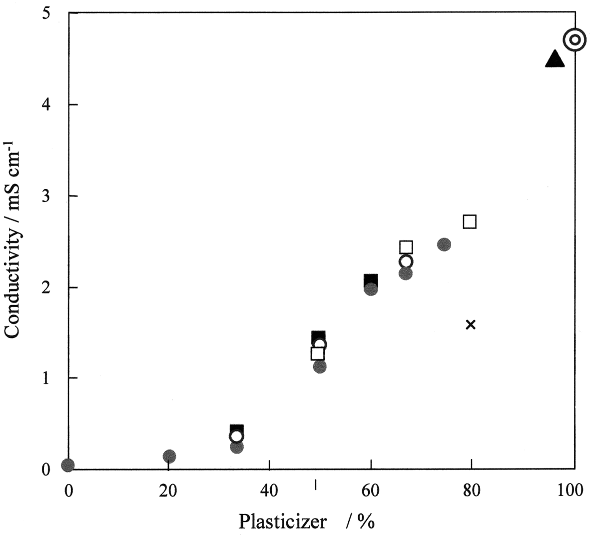


Fig. 5. Dependence of the conductivity on the content of the plasticizer. double circle: liquid electrolyte, closed circle: MMO/AAO = 6/4, open circle: MMO/AAO = 7/3, closed square: MMO/AAO = 8/2, open square: MEA/AAO = 9/1, closed triangle: Gelator, cross bar: MHH.

The flexible structure of the polymer, which is important for obtaining the high conductivity,[15] is achieved by the low extent of cross-linking and the high content of the plasticizer in the polymer electrolyte. In the following study, we selected an optimum content of the plasticizer: 75% of plasticizer for MMO and 80% of plasticizer for MEA.

Solid-State TiO_2 Solar Cells. Performances of Solid-State TiO_2 Solar Cells. The current-voltage characteristics of the solid-state TiO_2 solar cells containing the following polymer electrolytes were measured (Fig. 6) and the performance parameters were determined as listed in Table 1.

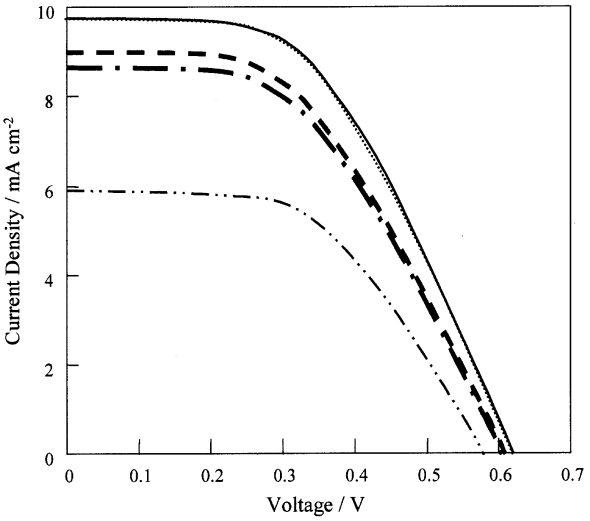


Fig. 6. Photocurrent-voltage characteristics of the solid state solar cells. broken line: polymer 1, point dotted line: polymer 2, solid line: liquid electrolyte, dotted line: gelator, two point dotted line: PMHH.

The cell using polymer 2 gave the highest efficiency among the three, which reached to 86.4% of that for the cell using the liquid electrolyte. The open circuit voltages of the cells using polymer 1 and 2 were comparable to that of the cell using the liquid electrolyte, while the short circuit current densities were lower by 0.7–1.1 mA cm^{-2}. These cells showed the comparable fill factor values to that for the cell using the liquid electrolyte. In the case of using PMHH, which was constructed with 20% of poly(MHH) and 80% of MPN, the performance was worse than the cell using the other polymer electrolytes. This low performance should be attributed to the high extent of cross-linking of the polymer which resulted from the presence of hydroxy groups at the end of side chains.

Figure 7 shows a relationship between the conductivity of the employed polymer electrolytes (shown in Fig. 5) and the short circuit current densities. A tendency can be seen that the higher short circuit current density was observed for the polymer electrolytes having the higher conductivity. The same trend was observed also for the relationship between the conductivity and the energy conversion efficiency (Table 1). These results led us to the conclusion that the conductivity of the electrolyte is a key factor determining the performance of the cell.

Series Resistance of the Cell. Solar cells working on a principle of the P–N junction can be treated as an equation circuit consisting of a rectifier and a constant current generator. The relationship between the current and voltage is given by Eq. 2 using photoinduced current Isc and Shockley's law (Eq. 1), which describes the characteristics of rectification of the P–N junction.[17]

$$I_d = I_0 [\exp (qV/nkT) - 1] \tag{1}$$

$$I = I_{sc} - I_d = I_{sc} - I_0 [\exp (qV/nkT) - 1] \tag{2}$$

For an actual cell, Eq. 3 is derived from Eq. 2 considering a series resistance (*Rs*) and parallel resistance (*Rsh*) in the cell.

$$I = I_{sc} - I_0 [\exp (q(V + Rs \cdot I)/nkT) - 1] - (V + Rs \cdot I)/Rsh \tag{3}$$

Equation 3 can be approximated as Eq. 4 when it is irradiated by strong light, since Id >> $(V + Rs \cdot I) / Rsh$.

$$I = I_{sc} - I_0 [\exp (q(V + Rs \cdot I)/nkT) - 1] \tag{4}$$

The porous TiO_2 electrode is considered to be an Schottky-type rectifier, as judged from its current-voltage characteristics in the dark. The dye-sensitized photoinduced current is also regarded as a constant current generator. Therefore, the photovoltaic characteristics of the dye-sensitized TiO_2 solar cell should be treated by Eqs. 3 or 4 as that of P–N junction solar cells. The pictorial diagram of the dye-sensitized TiO_2 solar cell and its equivalent circuit are shown in Fig. 8a and b, respectively. The series resistance *Rs* of the cell is considered to consist of the resistance of porous TiO_2 electrode (*Rs*–TiO_2), the resistance of the electrolyte (*Rs*- electrolyte) and the sheet resistance of the conducting glass (*Rs*-OTE).

The relationship between the current density and the voltage obtained by fitting with Eq. 4 for the cell which is constructed

Table 1. Performances of the Solid-State Solar Cells[a)]

Solvent	Conductivity[b)]	*Voc*[c)]	Isc[d)]	ff[e)]	η[f)]	*Rs*[g)]	*Rsh*[h)]
	$\mathrm{mSC\,m^{-1}}$	V	$\mathrm{mA\,cm^{-2}}$		%	Ω	$\mathrm{k\Omega}$
Polymer 1[i)]	2.36	0.61	8.61	0.49	2.53	26.0	15.5
Polymer 2[j)]	2.67	0.61	8.96	0.48	2.62	25.4	15.9
Solution	4.70	0.62	9.73	0.50	3.03	22.0	17.4
Gelator[k)]	4.70	0.62	9.73	0.50	2.99	22.5	17.3
PMHH[l)]	1.60	0.58	5.89	0.53	1.81	29.9	13.7

a) Under irradiation of AM 1.5, 1000 $\mathrm{W\,m^{-2}}$ simulated solar radiation. b) Conductivity of employed electrolytes. c) Open circuit voltage. d) Short circuit current density. e) Fill factor. f) Energy conversion efficiency. g) Series resistance of the cell. h) Parallel resistance of the cell. i) MMO/AAO/MPN = 6/4/30. j) MEA/AAO/MPN = 9/1/40. k) Gelaor 40 $\mathrm{g\,l^{-1}}$. l) MHH/MPN = 1/4.

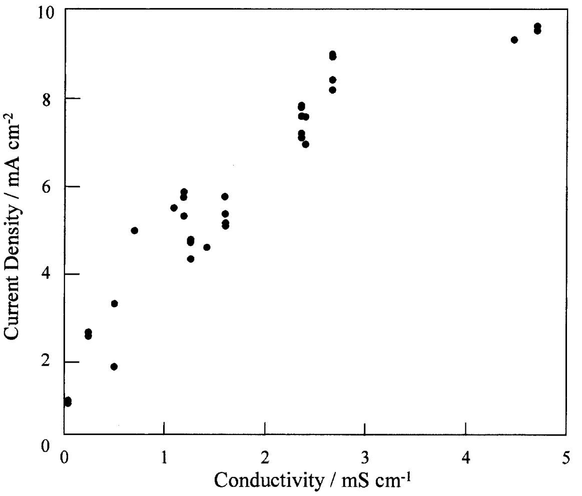


Fig. 7. Relationship between the conductivity of the polymer electrolytes and the short circuit current density of the solid-state solar cells.

with polymer 1 is shown in Fig. 9 as a typical example. The values of the saturation current I_0, the identical factor *n*, the series resistance *Rs* and the parallel resistance *Rsh* were estimated to be 0.86 nA, 1.46 Ω, 25.3 Ω, and 15.5 kΩ from this fitting. The estimated *Rs* and *Rsh* values are listed for the cells constructed using the three polymers, the gelator, and the liquid electrolyte in Table 1. The values of the parallel resistance *Rsh* were much larger than the series resistance *Rs* in all the cells, indicating that the back electron transfer was effectively suppressed.

Figure 10 shows the relationship between the estimated values of the series resistance *Rs* and the experimentally determined resistivity of the employed polymer electrolytes. The linear relationship was clearly observed, giving a slope and intercept as 0.015 $\mathrm{cm^{-1}}$ and 19.9 Ω, respectively (see the equation shown in the figure). The first term of the equation should correspond to the resistance of electrolyte (*Rs*-electrolyte), and then the apparent thickness T_{obs} (in the unit of cm) of the electrolyte layer can be estimated as the slope value, i.e., 1.5×10^{-2} cm (150 μm).

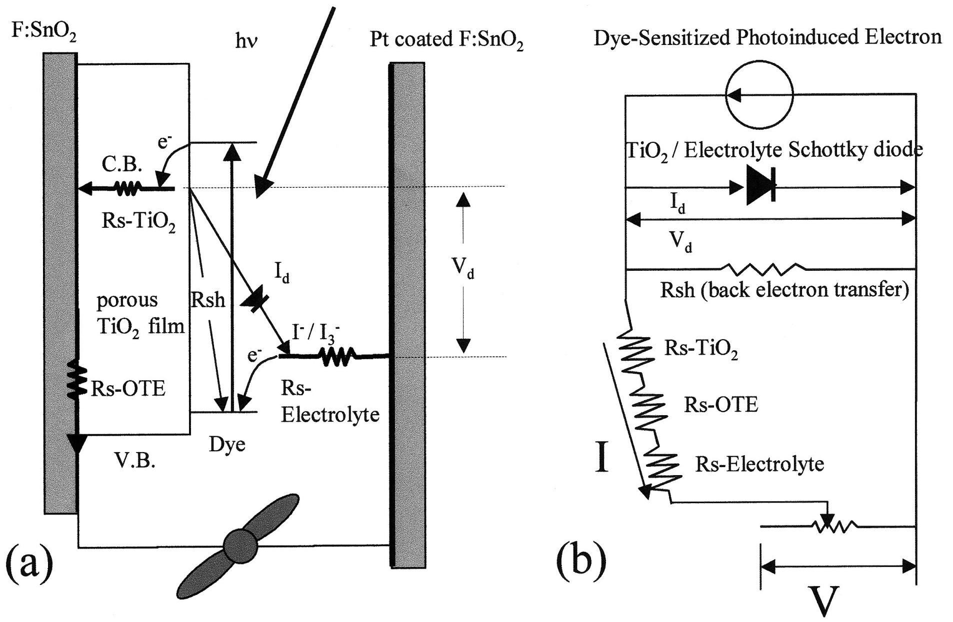


Fig. 8. The pictorial diagram of the dye-sensitized TiO_2 solar cell (a) and its equivalent circuit (b).

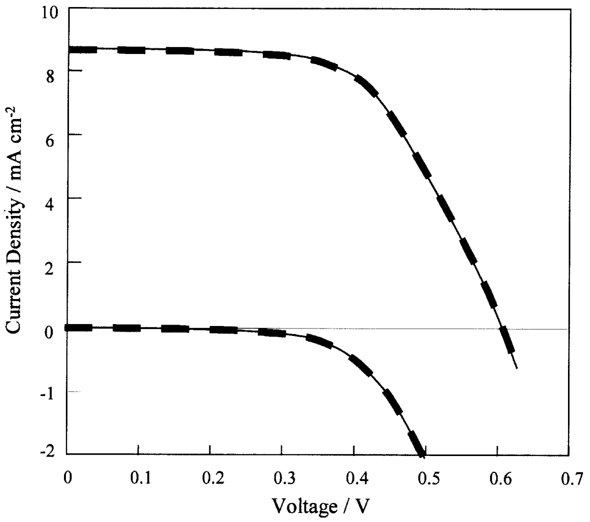


Fig. 9. Simulated current- voltage curve for the cell using the polymer 1. solid line: experimental data, dotted line: simulated curve.

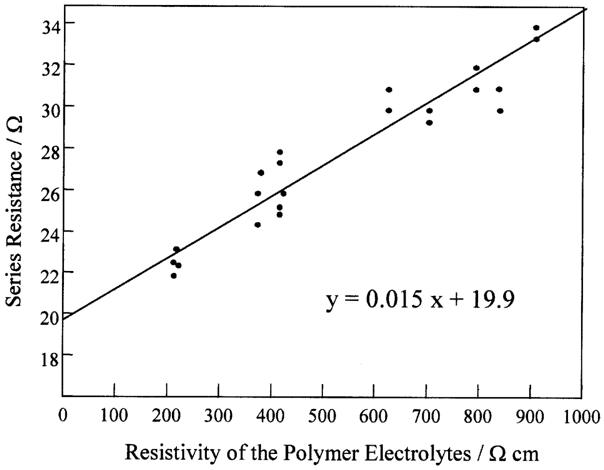


Fig. 10. Relationship between the series resistance of the cells and the resistivity of the polymer electrolytes.

$$T_{obs} = T_{free} + T_{in\ TiO_2} \qquad (5)$$

where T_{obs}: observed thickness, T_{free}: thickness of free electrolytes, T_{inTiO_2} : thickness of electrolytes in the porous TiO_2 electrode. This thickness of the electrolyte present in the TiO_2 film was estimated as 60 μm by subtracting the thickness of the space for the polymer electrolyte (90 μm) from the estimated thickness (150 μm) corresponding to the entire hole transporting layer. Interestingly, this value was 5 times larger than that of the geometric thickness of the TiO_2 electrode (12 μm). This analysis suggests that the polymer electrolyte exists and works as a hole-transporting layer even in the labyrinth of the nanoporous TiO_2 film. The intercept of the equation should indicate the sum of the resistance of TiO_2 (*Rs*-TiO_2) and the resistance of the conductive glass (*Rs*-OTE). As the sheet resistance of employed OTE was 10 Ω/□, the resistance of TiO_2 was estimated to be 9.9 ς, giving the conductivity of the porous TiO_2 electrode as 0.12 mS cm^{-1}. This value was much higher than that reported for TiO_2 under photo-irradiation (ca. 50–800 nS cm^{-1})[18] and should be more investigated for better understanding.

Conclusions

A solid-state dye-sensitized TiO_2 solar cell has been fabricated with the polymer electrolyte, which is prepared by the *in-situ* polymerization method and the immersion introduction technique. The energy conversion efficiency of the solid-state cell has been 2.62% under irradiation of simulated sunlight (AM 1.5, 1 kW m^{-2}), which is 86.4% of the efficiency of the liquid electrolyte cell (3.03%). Considering the previous study on the long-term durability of the polymer-electrolyte TiO_2 solar cell,[6b] which provides 1.62% with over 8000 h stability, the *in-situ* preparation of the polymer electrolyte followed by *in-situ* immersion of the redox electrolyte have been demonstrated to be promising for fabrication of the solid-state TiO_2 solar cells with the improved conversion efficiency and long-term stability. The conductivity of the TiO_2 electrode was estimated to be 0.12 mS cm^{-1} by the analysis using the equivalent circuit and the equation employed for P–N junction solar cells.

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