

Quasi-solid dye-sensitized solar cells containing chemically cross-linked gel

How to make gels with a small amount of gelator

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Abstract

Quasi-solid dye-sensitized solar cells equipped with chemically cross-linked gels are reported. The gelator contains multi-functional pyridine or imidazole derivatives and multifunctional halogen derivatives. The former reacts with the latter to give three-dimensional ionomer structures even in liquid electrolytes. Gelators polymerized directly in liquid electrolytes of cells have not been reported so far. This makes the cell fabrication process easier, where electrolyte precursors are injected into cells, followed by gelled directly in the cells. In addition, a micro-phase separation technique is introduced in order to decrease the amount of gelators. This makes it possible for the liquid electrolytes to be solidified without losing the high performance of liquid-type cells before gelation. © 2002 Published by Elsevier Science B.V.

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1. Introduction

Dye-sensitized solar cells (DSCs) are filled with liquid electrolytes [1,2] containing volatile organic solvents. Solid electrolytes should increase long-term stability associated with solvent evaporation and decrease the risk of solvent leakage when the cell was broken. In spite of extensive researches, the performance of solid DSCs is not satisfactory. This has been partially explained by imperfect contact between solid electrolytes and nanoporous TiO₂ layers [2–5]. Gel electrolytes are solid visually, but contain liquids in polymer matrixes [6–8]. Therefore, gel electrolytes should improve these contacts. Actually, quasi-solid DSCs (Q-DSCs) containing physical gels have been reported to have almost the same performance as those containing liquid electrolytes before gelation. Physical gels become liquid states again when they are heated. Thermally stable chemically cross-linked gels for DSCs have not been reported except for one report using a complicated method [2–4].

Extensive works on gel electrolytes have been done in the field of lithium ion batteries [9–12]. The addition of acrylic monomers (gelators) and radical initiators in liquid elec-

trolytes followed by cross-linking is the most convenient method to make gel electrolytes. This method was not able to be applied to DSCs because iodine inhibited the cross-linking reactions. Another gelation method has to be found. In addition, gelators in electrolytes are inactive electrochemically. Therefore, the amount of the gelator should be as small as possible.

Our purpose is to propose the method realizing chemically cross-linked gel electrolytes having the performance which is almost the same as that of the corresponding liquid electrolyte. We focused on the gelation method itself and how to decrease the amount of the gelator.

2. Experimental

2.1. Material

cis-Di(thiocyanato)-*N,N'*-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid) ruthenium(II) complex and TiO₂ past (Ti-nanoxide) were purchased from Solaronix SA. Fluorine-doped SnO₂-layered glass plates (10 Ω/□)(SnO₂/F) were purchased from Asahi Glass. Polyvinylpyridine (BB1), polyacrylate, ZnCl₂, CL1 are commercially available (Wako Pure Chemicals) and were used without further purification. Molecular weights for polyvinylpyridine (BB1) used were

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Table 1
Composition of gel electrolyte precursors (pre-GE)^a

Number	Multi-functional polymer		CL1 (wt.%)	ZnCl ₂ (wt.%)	I ₂ (mM)
	Compound	(wt.%)			
G1	BB1 (MW 160 000)	1	3.5	–	100
G2	BB1 (MW 60 000)	1	3.5	–	100
G3	BB1 (MW 1350)	1	3.5	–	100
G4	BB2	1.7	2	–	100
G5	–	–	–	–	100
G6	BB3 (MW 2500)	1.25	–	1.25	100
G7	BB3 (MW 50 000)	1.25	–	1.25	100
G8	BB3 (MW 100 000)	1.25	–	1.25	100

^a Ref. 1: Acetonitrile+0.5 M LiI+0.3 M HMII+0.58 M TBP+50 mM I₂. HMII: 1-hexyl-3-methylimidazolium iodide; TBP: 4-*tert*-butylpyridine.

160 000, 60 000 and 1350, and those for polyacrylate (BB3) were 100 000, 50 000 and 2500, respectively.

BB3 was synthesized by reacting the polyacrylic acid with tetraethylammonium hydroxide in water. After the reaction, the water was removed under vacuum and BB3 was obtained as a white powder and used without further purification.

The gel electrolyte precursors contain gelators, iodine and imidazolium iodide mixtures as the main compositions. The compositions are summarized in Table 1.

Synthesis [13] of BB2: NaOH (28 g, 0.70 mol) was dissolved in dimethylsulfoxide (300 ml). Imidazole (52 g, 0.76 mol) was added to the mixture and heated at 100 °C for 1 h. Then, 1,2,4,5-tetrakis(bromomethyl)benzene (40 g, 0.089 mol) was added at 100 °C for 2 h. After the reaction completed, solvents were removed from the reaction mixture under vacuum. The crude product was viscous oil. Celite (Aldrich, Diatomaceous) and methanol were added to the viscous oil in order to make a uniform dispersion. The methanol was removed under reduced pressure. The residual white powder was washed with 2-propanol to eliminate NaBr and other byproducts. The product adsorbed on the Celite was extracted by washing the powder with ethanol. After the filtration, the ethanol solution was concentrated under reduced pressure. The residue was crystallized from acetone to give white crystal (BB2): 33.6 g, yield, 95%. ¹H NMR (270 MHz, CDCl₃): δ 5.271 (s, 8H), 6.703 (s, 2H), 6.929 (s, 4H), 6.975 (s, 4H), 7.588 (s, 4H) ppm; ¹³C NMR (67.5 MHz, CDCl₃): δ 48.80, 121.66, 130.46, 130.77, 137.45, 139.51 ppm.

2.2. Fabrication of photo-electrochemical cell

Dye-anchored porous TiO₂ electrodes (1 cm²) were prepared using *cis*-di(thiocyanato)-*N,N'*-bis(2,2'-bipyridyl)-4,4'-dicarboxylic acid)ruthenium(II) complex, TiO₂ past and a fluorine-doped SnO₂-layered glass plate as reported previously [1]. Counter-electrodes were prepared by sputtering Pt on SnO₂/F-layered glass plates (Nippon Sheet Glass). An adhesive (Sulyn, Dupont) was inserted between the TiO₂ and the counter-electrodes as spacer. The gap was controlled to

be about 20 μm. Then, gel electrolyte precursors (pre-GE) were injected into spaces between the two plates at room temperature. Then, the cell was placed in a 80 °C oven for 0.3 h to complete the gelation.

2.3. Conductivity

Electrolytes were injected into two metal plates (1 cm²) in which a spacer (0.1 cm) was set. Conductivity was measured with an impedance analyzer (Hewlett Packard, model HP4192A) at 500 kHz, tentatively.

2.4. Photo-current measurement

Photo-electrochemical measurements were performed using AM1.5 solar simulator (WXS-R50S-1.5, Maki Manufacturing) furnished with a Xenon lamp. The light intensity was monitored with a polysilicon illuminometer standardized by Japan Quality Assurance Organization (JQA). The photovoltaic performance depends on how to make cells and their conditions. Therefore, the performance of various cells was compared each other in the same series of experiments.

2.5. Apparatus

¹H NMR spectra were recorded on a JEOL model GSX-270 spectrometer, and all NMR data were reported in ppm (δ) down-field from tetramethylsilane. The viscosity of electrolytes at a temperature of 25 °C was measured by making use of a Tokyo Keiki ELD viscometer.

3. Results and discussion

3.1. Gelation reaction

In order to make gels, polymers have to grow in liquid electrolytes. The following items are necessary:

- 1) Polymerization occurs in the presence of iodine.
- 2) Polymerization occurs at the temperature below 100 °C.
- 3) Polymerization should initiate and complete even under some impurities such as oxygen, water, ions and so on.
- 4) Polymerization has to complete without generating byproducts decreasing PV performance.
- 5) Polymerization proceeds without initiators because the resultant decomposition products of the initiator may decrease PV performance.

From the above point of views, we selected addition reactions to make ionomers, as shown in Fig. 1.

Gelations 1 and 2 are addition reactions and do not generate any byproducts. Gelation 3 is a kind of condensation polymerizations and the polymerization proceeds, generating small molecules. However, gelation 3 is designed that the resultant molecules become ammonium iodide ions, one of electrolyte compounds commonly employed for DSCs.

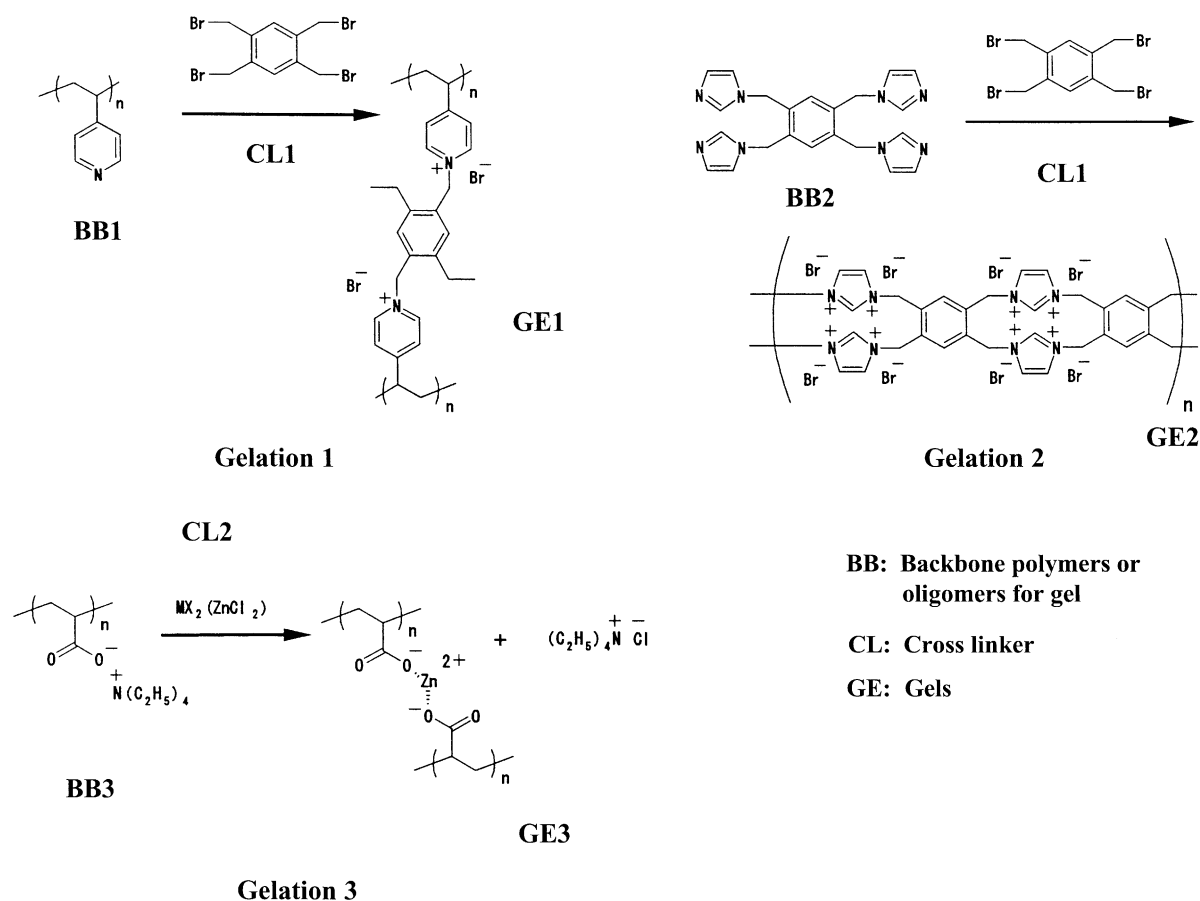


Fig. 1. Reaction mechanisms for gelation and abbreviations for compounds used.

3.2. Composition of gel electrolyte precursors (pre-GEs)

Pre-GEs composed of liquid electrolytes and gelators. Gelators have two components, namely multi-functional polymers or oligomers (BB) to make gel backbones, and cross-linkers (CLs) as shown in Fig. 2. The electrolyte contains 0.1 M iodine and molten salt mixtures as the main components. The compositions for pre-GEs and these abbreviations are summarized in Table 1 and Fig. 1. In order to examine whether compositions gel or not, the amount of CL1 was kept at 3.5 or 2% while the amount of BB1 or

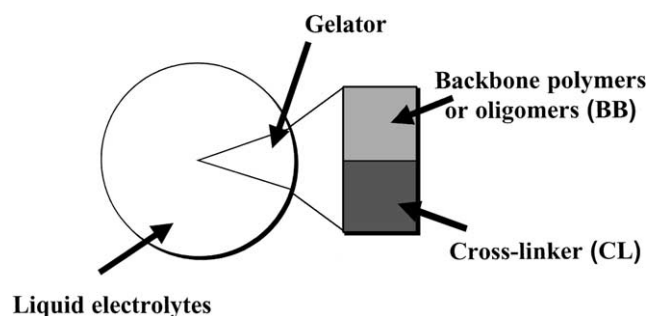


Fig. 2. Composition of gel electrolyte precursor (pre-GE).

BB2 was changed from 20 to 1%. The detail is described in Section 3.3 and Fig. 5. Therefore, the values of BB1 and BB2 in Table 1 show the minimum amount of BB1 and BB2 for the composition to be gelled.

3.3. Gel electrolyte fabrication process

Gel formation is carried out in the PV cell, as shown in Fig. 3. Gel electrolyte precursors containing liquid electrolytes and gelators are injected into PV cells already set. The gelation is carried out in the cell by heating the cell at 80 °C.

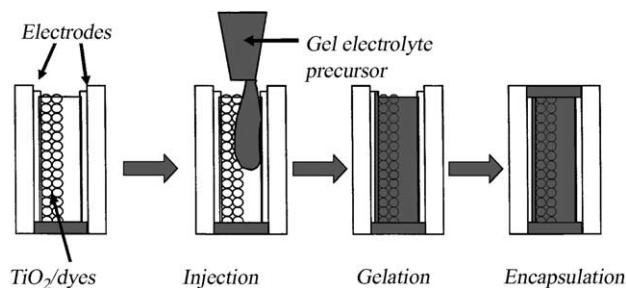


Fig. 3. Process for fabrication of quasi-solid DSCs.

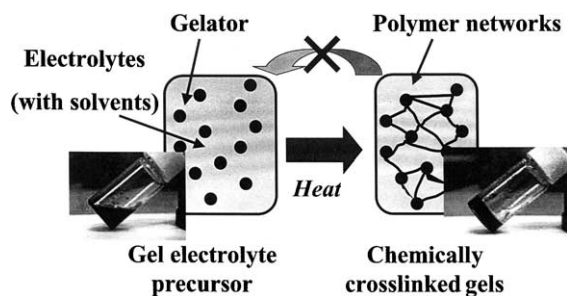


Fig. 4. Brief reaction mechanism of chemically cross-linked gel electrolytes.

Pre-GEs are liquid at first. This makes it possible for the pre-GEs to be impregnated into nanoscale pores of TiO₂ layers. By heating, gelators propagate three-dimensional polymer networks in the cell. These networks are made with covalent bonds and never return to liquid states even if the gel electrolytes are heated. A brief image is described in Fig. 4. In this process, when much gelator was added in the liquid electrolytes, the initial viscosity increases and the conductivity of the gel electrolytes would decrease because gelators are commonly electro-inactive. Both should decrease DSC performances. Therefore, to find methods to gel liquid electrolytes with the small amount of gelators are crucial. We found that a micro-phase separation technique is useful as is discussed in the following section.

3.4. Gelation with micro-phase separation

Low molecular weight gelators have an advantage over high molecular weight gelators, because the initial viscosity of the former is lower. The disadvantage of the former is that we need a large amount of the gelator. We found that the amount of gelators can be decreased by using uniform micro-phase separation. The micro-phase separation can be realized by using BB2 and CL1 (gelation 2 in Fig. 2). The pre-GE was transparent liquid. However, during the gelation, the gelator is gradually and uniformly phase-separated from liquid electrolytes and the gel electrolyte becomes turbid. Gel electrolyte GE2 can be obtained by adding only 3.7% of gelators into the liquid electrolyte (Table 1, G4). In contrast, more than 8.6% of BB2 and CL1 was needed to gel in an electrolyte which does not cause the micro-phase separation as shown in Fig. 5. In Fig. 5, the composition of these liquid electrolytes was changed to cause different polymer–electrolytes interaction. In order to obtain the micro-phase separation, the interactions between gelators and liquid electrolytes have to be optimized. When the gelators interact with the liquid electrolyte too well, the resultant gel electrolyte is homogeneous and much gelator is needed. When the interaction between the gelator and the electrolyte is too poor, the gelator reacts by itself and the electrolyte is left as it is, resulting in complete two-phase separation. The reason why the micro-phase separation is effective to

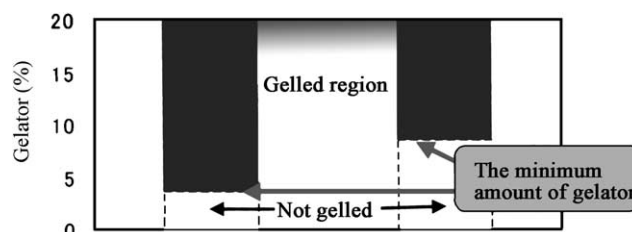


Fig. 5. The minimum amount of gelator in phase-separated gel and in homogeneous gel. Gelator contains backbone polymer (oligomer) and cross-linker. In order to find the minimum amount, the equimolar amount of CL1 and BB2 were added, and the total amount was changed from 20 to 1%.

decrease the amount of gelators can be explained by an assumption that reaction points become concentrated in the polymer-rich phase and the cross-linking reaction proceeds well, compared with homogeneous gels, where the reaction points are dispersed in all area of the electrolytes.

To use high molecular weight backbone polymers is useful for making gels with toughness. However, the addition of the high molecular weight polymers increases the viscosity of the pre-GEs. We found that the micro-phase separation technique is also useful for decreasing the amount of high molecular weight backbone polymers. We focused on the relation between the molecular weight of the gelator and initial viscosity of gel electrolyte precursors. Fig. 6 shows the relation between the minimum amount of the backbone polymer (polyvinylpyridine) to make gels and the molecular weight. The amount of the cross-linker (CL1) was fixed at 3.5 wt.%. The amount of the backbone polymer decreased slightly with an increase in the molecular weight as shown in Fig. 6. The amount was, however, small, 1–2 wt.% in the whole range of molecular weights. Because of this, the viscosity increase in the initial gel electrolyte precursor was kept low even when high molecular weight backbone polymers were employed.

Fig. 7 shows gel electrolytes prepared by using a low molecular weight backbone polymer and a high molecular

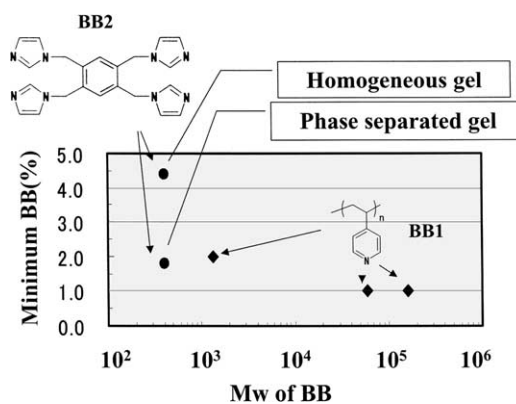


Fig. 6. Relationship between the minimum amount of backbone polymers in gelators and the molecular weight of the backbone polymer.

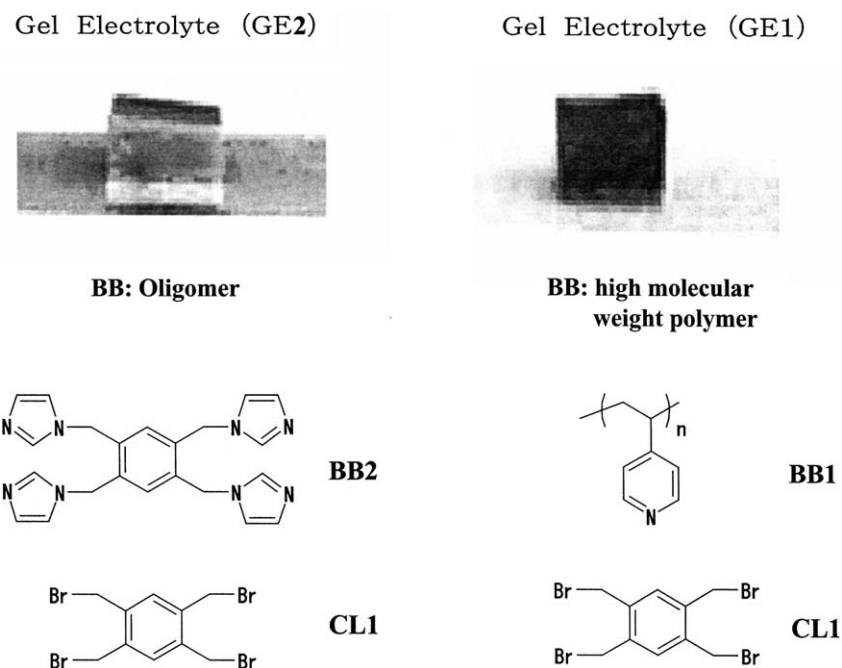


Fig. 7. Pictures of phase-separated gels and transparent gels. Right: phase-separated gel electrolyte (G4); left: transparent gel electrolyte (G1).

weight polymer. Gels can stand by themselves. Liquid electrolytes do not come off from the gels. These gels kept the shape even when the temperature increased to 80 °C, while the gel electrolyte obtained by using polyacrylonitrile as a gelator became fluid state at the temperature. These results proved the high heat-resistant properties for chemically cross-linked gels.

Fig. 8 shows the relation between viscosity and the molecular weight of backbone polymers (BB) when the minimum amount of the gelator was used in each composition. The viscosity increased gradually with an increase in the molecular weight. The viscosity of the pre-GE using BB2 was half of that using the highest molecular weight backbone polymer.

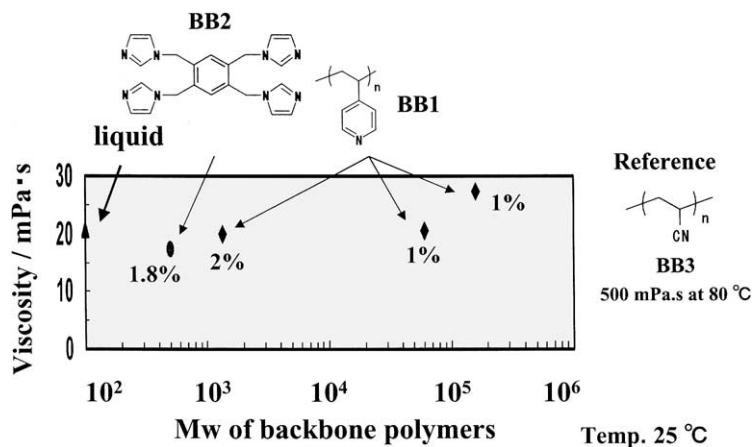


Fig. 8. Relationship between viscosity and molecular weight of backbone polymers or oligomers at 25 °C. The viscosity was measured after backbone polymers were added to the liquid electrolyte. Cross-linkers were not added.

Pre-GEs causing phase separations should have an advantage in terms of the electrolyte injection process. These pre-GEs had much lower viscosity, compared with that containing polyacrylonitrile (PA), a conventional physical gelator.

3.5. Properties of gel electrolytes

Fig. 9 shows the relation between the conductivity and the molecular weight of backbone polymers (BB) when the minimum amount of the gelator was used in each composition. Conductivities for gel electrolytes were between 8 and 10 mS/cm and large variations were not seen, depending on the structure of gels and molecular weights of the

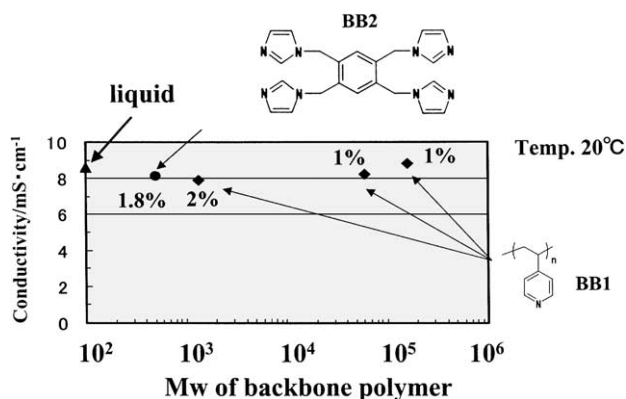


Fig. 9. Relationship between conductivity of gel electrolytes and molecular weight of backbone polymers in pre-GE. For measurement, see Section 2.

backbone polymers. Any decrease in the conductivity was not observed after gelation, compared with the corresponding liquid electrolyte before gelation.

Fig. 10 shows the short circuit current density of DSCs filled with various gel electrolytes. The abscissa shows the molecular weight of backbone polymers or oligomers. The current density was also between 8 and 10 mA/cm² in the series of this experiment. Large variations were not observed, depending on the molecular weight of the backbone polymers or oligomers, because the amount of these gelators kept low in the whole molecular weight region. The large decrease in the conductivity was not observed after the gelation, compared with the corresponding liquid electrolyte before gelation. These results show that the gelator is solid visually, but the electrolyte behaves like liquid states.

Fig. 11 shows the results when performance of DSCs after and before gelation, and a liquid electrolyte based on acetonitrile (Ref. 1 in Table 1) were compared with each other. The values themselves are different from those in Fig. 10, because these values vary in each experiment. We are not able to explain the reason. However, when these experiments were carried out in series, the reproducibility was not bad.

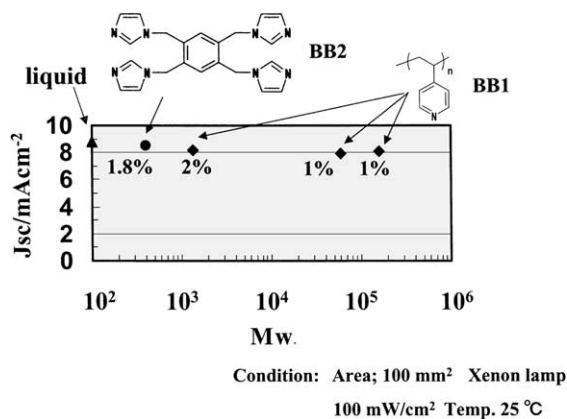


Fig. 10. Relationship between J_{sc} of DSCs and the molecular weight of backbone polymers in pre-GE. For measurement, see Section 2.

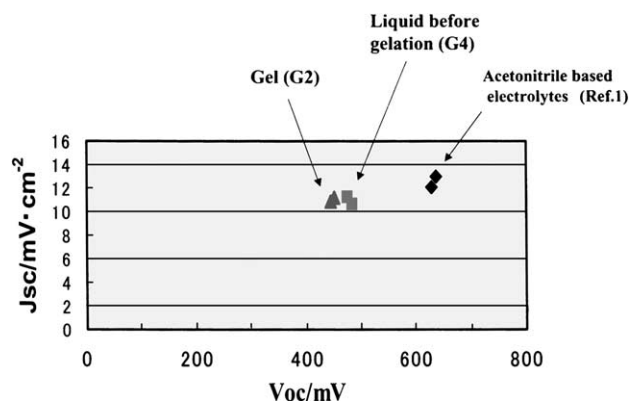


Fig. 11. Performance of DSCs containing liquid electrolytes and the corresponding gel electrolytes (G2). For measurement, see Section 2. Cell area: 1 cm² at 25 °C. The performance of DSCs containing acetonitrile as the solvent (Ref. 1) is also shown in this figure. The composition was summarized in Table 1. The values themselves are different from those in Fig. 10, because these values vary in each experiment. Data in Fig. 11 were taken consecutively to compare quasi-solid DSCs with DSCs before gelation and DSCs containing acetonitrile, a conventionally employed solvent.

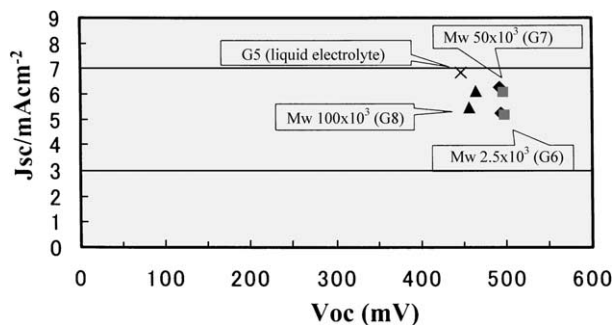


Fig. 12. Performance of DSCs containing liquid electrolytes and the corresponding gel electrolytes (G6, G7 and G8). The composition was summarized in Table 1. Cell area: 1 cm² at 25 °C.

Therefore, data on the same figure are always the values obtained by the experiments made in series. The J_{sc} and V_{oc} before gelation were almost the same as those after gelation. The current density was close to that for the DSC containing acetonitrile in the liquid electrolyte (Ref. 1). We are now trying to increase the V_{oc} .

Fig. 12 shows the PV performance filled with G3 gel. A large decrease in the PV performance was not observed after gelation. There was no relation between the molecular weight of BB3 and the PV performance. In these gel electrolytes, the amount of the gelator was kept low at 3%.

4. Conclusions

Ionomers turned out to be a useful structure for gelator in liquid electrolytes containing iodine. The amount of the gelator was able to be decreased by using a phase separation

technique during the gelation or by using high molecular weight backbone polymers. These techniques minimized the amount of the backbone polymer to 1–2 wt.% and prevented the decrease in the PV performance after gelation. Heat-resistant property of chemically cross-linked gel electrolytes was proved to be higher than those of physical gels.

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