

***In Situ* Crosslinked Ionic Gel Polymer Electrolytes for Dye Sensitized Solar Cells**

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Abstract: We prepared an ionic gel polymer electrolyte for dye-sensitized solar cells (DSSCs) without leakage problem. Triiodide compound (BTDI) was synthesized by the reaction of benzene tricarbonyl trichloride with diethylene glycol monotosylate and subsequent substitution of tosylate by iodide using NaI. Bisimidazole was prepared by the reaction of imidazole with the triethylene glycol ditosylate under strongly basic condition provided by NaH. BTDI and bisimidazole dissolved in an ionic liquid were injected into the cells and permeated into the TiO₂ nanopores. *In situ* crosslinking was then carried out by heating to form a network structure of poly(imidazolium iodide), thereby converting the ionic liquid electrolytes to a gel or a quasi-solid state. A monomer (BTDI and bisimidazole) concentration in the electrolytes of as low as 30 wt% was sufficient to form a stable gel type electrolyte. The DSSCs based on the gel polymer electrolytes showed a power conversion efficiency of as high as 1.15% with a short circuit current density of 5.69 mAcm⁻², an open circuit voltage of 0.525 V, and a fill factor of 0.43.

Keywords: dye sensitized solar cells, ionic gel polymer electrolytes, *in situ* crosslinking, quasi-solid state.

Introduction

Dye sensitized solar cell (DSSC) developed by Grätzel is based on the mechanism of a regenerative photoelectrochemical process.^{1,2} In the cell, a dye sensitizer is excited by an incident photon and injects an excited electron to the conduction band of nanocrystalline TiO₂. Since it has achieved high power conversion efficiency reaching 11% at a low manufacturing cost, DSSC has received much attention from the industrial sectors as well as the academic communities as a promising next generation of solar cells.^{3,4} Now, long-term durability remains one of the challenging issues mostly due to evaporation of volatile organic solvents and leakage of liquid electrolytes.

Ionic liquids such as imidazolium iodides, which are a molten salt at room temperature, are an attractive electrolyte for replacement of the volatile organic solvents due to their very low vapor pressure and high ionic conductivity. The ionic liquids could be quasi-solidified by mixing with a certain precursor material and subsequent chemical or physical cross-linking. The resulting ionic gels or ionic polymer electrolytes are recognized promising candidate of electrolytes for DSSCs with durability and stability due to their non-vol-

atility and non-flammability, chemical and thermal stability and relatively good ionic conductivity. Several researchers demonstrated such solidified ionic electrolytes by incorporating various materials such as poly(vinylidene fluoride-co-hexafluoro propylene), polyvinylpyridine, poly(imidazolium iodide), etc.⁵⁻⁸ Among them, poly(imidazolium iodide) suggested by S. Yanagida *et al.* which is an ionic salt polymer prepared by thermal polymerization between bisimidazoles and alkyl diiodide, is quite interesting because it acts as a gelator and also contributes ionic conductivity.⁸

In this work, we prepared the DSSCs based on an ionic gel polymer electrolyte derived from *in situ* crosslinking of aromatic triiodide compound and bisimidazoles dissolved in the ionic liquid of imidazolium salt. Aromatic triiodide is expected higher crosslinking efficiency and also higher thermal stability compared with the alkyl diiodide. The polymer electrolytes, once cured, have difficulty in permeating into the pores of nanocrystalline TiO₂ electrodes due to its quasi-solid state. So, we soaked the nanoporous TiO₂ electrodes in the solution of the precursor electrolytes and then thermally cured it, resulting in quasi-solidified polymer electrolytes. The performance of the resulting DSSCs was evaluated by using the gel polymer electrolytes at different concentrations of the gelating monomers (aromatic triiodide compound and bisimidazoles).

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Experimental

Materials. Diethylene glycol, imidazole, benzene tricarbonyl trichloride, lithium iodide, platinum (IV) chloride, iodine and sodium iodide were purchased from Aldrich Co. Triethylene-glycol-di-*p*-tosylate was purchased from TCI Co. TiO₂ suspension (Nanoxide T), Surlyn film (25 μm), ruthenium 535 dye (N3), propyl-methyl-imidazolium iodide (PMII) were purchased from Solaronix SA and were used as received. The transparent conducting oxide glass substrate was purchased from Pilkinton (TEC-8, fluorine doped SnO₂ coated glass).

Synthesis of Diethylene Glycol Monotosylate. Sodium hydroxide (7.5 g, 0.188 mol) was dissolved in the mixture of tetrahydrofuran (80 mL) and water (80 mL) under nitrogen flow at 0 °C. Diethylene glycol (20 g, 0.188 mol) in tetrahydrofuran was added dropwise in the solution. After stirred for 30 min, *p*-toluene-sulfonyl chloride (17.8 g, 0.094 mol) was added dropwise. After the reaction was completed, the solution was poured into water and extracted with dichloromethane. After the solvent was evaporated, the residue was purified by column chromatography (ethyl acetate/hexane = 1/1) to obtain a colorless liquid (13.5 g) (yield: 55 %). ¹H-NMR (CDCl₃, ppm) δ 2.45 (s, 3H), 2.64 (s, 1H), 3.55 (t, *J* = 3 Hz, 2H), 3.69 (m, 4H), 4.18 (t, *J* = 3 Hz, 2H), 7.37 (d, *J* = 6 Hz, 2H), 7.79 (d, *J* = 6 Hz, 2H).

Synthesis of Benzene Tricarbonyl Diethylene Tosylate. Diethylene glycol tosylate (6.0 g, 23 mmol) and anhydrous triethylamine (2.33 g, 23 mmol) were dissolved in anhydrous dichloromethane at 0 °C. A solution of benzene tricarbonyl trichloride (2.04 g, 7.7 mmol) in dichloromethane was added dropwise into the solution. After stirred for 4 h, the resulting solution was poured into water and extracted with dichloromethane. After the solvent was evaporated, the residue was purified by column chromatography (ethyl acetate only) to produce a colorless liquid (5.0 g) (yield: 70%). ¹H-NMR (CDCl₃, ppm) δ 2.47 (s, 9H, CH₃), 3.75 (m, 12H), 4.18 (t, *J* = 3 Hz, 6H), 4.45 (t, *J* = 6 Hz, 6H), 7.32 (d, *J* = 6 Hz, 6H, aromatic proton), 7.79 (d, *J* = 6 Hz, 6H, aromatic proton), 8.84 (s, 3H, aromatic proton).

Synthesis of Benzene Tricarbonyl Diethylene Iodide (BTDI). Into a 250 mL three-necked flask equipped with a stirrer, condenser and nitrogen inlet, benzene tricarbonyl diethylene tosylate (4.8 g, 5.1 mmol), sodium iodide (5.73 g, 38 mmol) and 80 mL of anhydrous acetone were added. The solution was heated to reflux for 2 h and then cooled to room temperature. The resulting solution was poured into water and extracted with dichloromethane. After the solvent was evaporated, the residue was purified by column chromatography (ethyl acetate/hexane = 1/1) to produce a light yellow viscous liquid (2.6 g) (yield: 60%). ¹H-NMR (CDCl₃, ppm) δ 3.28 (t, *J* = 6 Hz, 6H), 3.81 (m, 12H), 4.55 (t, *J* = 6 Hz, 6H), 8.92 (s, 3H, aromatic protons). ¹³C-NMR (CDCl₃, ppm) δ 64.9 (3C, -COO-CH₂-), 68.9 (6C, -CH₂-O-CH₂-), 72.1 (3C, I-

O-CH₂-) 131.5 (3C, aromatic carbons), 135.3 (3C, aromatic carbons), 165.2 (3C, -COO-). FT-IR (neat on NaCl window, cm⁻¹): 2954 (m), 2869 (m), 1727 (vs), 1608 (w), 1446 (m), 1357 (w), 1241 (vs), 1110 (s), 1033 (m).

Synthesis of Bisimidazole. Into a 250 mL three-necked flask equipped with stirrer, condenser, nitrogen inlet, sodium hydride (1.44 g, 0.060 mol) and 50 mL of anhydrous tetrahydrofuran were added. Tetrahydrofuran solution of imidazole (3.40 g, 0.050 mol) was added slowly and stirred for 30 min at 50-60 °C. Triethylene glycol di-*p*-tosylate (11.46 g, 0.025 mol) in tetrahydrofuran was added dropwise and stirred for 12 h. After the solvent was evaporated, the residue was purified by column chromatography (acetone/methanol = 5/1) to produce a yellow liquid (4.0 g) (yield: 61%). ¹H-NMR (CDCl₃, ppm) δ 3.52 (s, 4H), 3.67 (t, *J* = 6 Hz, 4H), 4.08 (t, *J* = 6 Hz, 4H), 6.96 (s, 2H), 7.04 (s, 2H), 7.52 (s, 2H). ¹³C-NMR (CDCl₃, ppm) δ 47.6 (2C, N-CH₂-), 71.0 (4C, -CH₂-O-CH₂-CH₂-O-CH₂-) 119.9 (2C, imidazole), 129.6 (2C, imidazole), 138.1 (2C, imidazole). FT-IR (neat on NaCl window, cm⁻¹): 3112 (m), 2869 (m), 1670 (w), 1511 (vs), 1442 (m), 1357 (m), 1288 (m), 1234 (s), 1110 (vs), 1083 (vs), 1037 (m).

Preparation of Ionic Gel Polymer Electrolytes. A stock solution of ionic liquid was prepared by dissolving lithium iodide (0.04 g) and iodine (0.1 g) in PMII (1.0 g) and was kept in a desiccator. The ionic liquid was used as a reference electrolyte to compare with the gel polymer electrolytes. Precursor solution was obtained by dissolving the gelating monomers (BTDI and bisimidazole) in the above ionic liquid. The minimum monomer concentration was found to be 30 wt% to produce a firm gel by heating the precursor solution. We failed to obtain a gel at 20 wt%. To demonstrate the effect of the monomer concentration on the performance of the resulting ionic gel polymer electrolytes, the concentration was varied from 30 to 50 wt% to the total precursor solution. The mixing ratio of BTDI and bisimidazole was kept at 2/3 (mol/mol). The precursor solution was injected in DSSC device and then was cured by heating to produce an ionic gel. To find out the optimum curing condition, in which the precursor solution was completely gelated and hence did not show any flow, several processing conditions were tested. In case of 50 wt% of monomer concentration, the precursor was found to be firmly gelated at 100 °C in 4 h. At lower temperatures such as 70 and 80 °C, even more than 12 h heating did not lead to a complete gelation. The precursors with a lower concentration of the monomer required 30 min-1 h longer gelation time at 100 °C than 50 wt% of monomer concentration.

Measurements. ¹H-NMR and ¹³C-NMR spectra were obtained from a Bruker ARX-300 spectrometer at 300 and 75 MHz, respectively. FT-IR spectra were recorded using a Bruker vector / 22 Near-IR spectrometer.

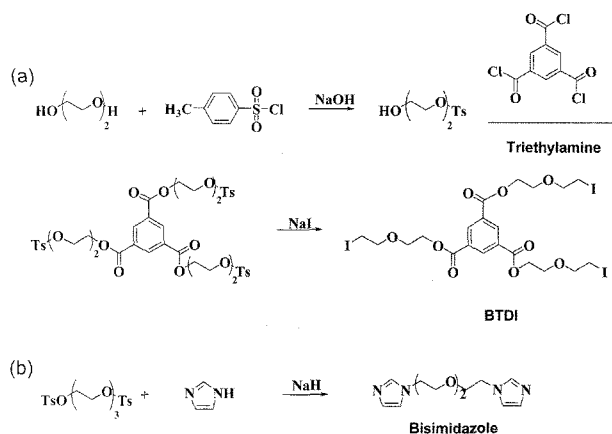
To evaluate ionic conductivity, the precursor of ionic polymer electrolytes were coated on the pre-patterned ITO substrates and gelated by heating.¹⁰⁻¹² Thickness of the resulting poly-

mer electrolyte was about 100 μm . The AC impedance of the conductivity of the sample was measured by impedance analyzer (Zahner Elektrik model IM6). The 50 mV of AC amplitude was applied with a frequency sweep from 1 Hz to 1 MHz with a controlled temperature by means of the programmable hot plate (Mettler, model FP 82HT).

A nanoporous TiO_2 colloidal paste (Ti-Nanoxide T, particle size: 13 nm, Solaronix SA) was coated on a fluorine-doped tin oxide glass (FTO glass) via a doctor-blade technique. After drying, the film was sintered at 450 $^\circ\text{C}$ for 3 h. The FTO glass substrate coated with the TiO_2 layer was immersed in a solution of dye (N3) at room temperature for 24 h. Platinum was deposited on another FTO glass by sputtering and the substrate was used as a counter electrode. Surlyn film (25 μm) was placed between the TiO_2 coated substrate and platinum coated one, then the precursor solution was injected to fill the gap between the two substrates. The overall device structure was FTO / TiO_2 / N3 / electrolyte / platinum / FTO. After the polymer electrolyte precursor was injected in DSSC device, the assembled solar cell was cured at 100 $^\circ\text{C}$ for 4-5 h. Photocurrent-voltage curves were measured at room temperature under AM 1.5 simulated sunlight (100 mWcm^{-2}), in which the area of the TiO_2 photoelectrode was 0.25 cm^2 .

Results and Discussion

The triiodide compound (BTDI) was synthesized by the reaction of benzene tricarbonyl trichloride with diethylene glycol monotosylate and subsequent substitution of tosylate by iodide using NaI as shown in Scheme I. BTDI has an aromatic ring as a core unit attached with three branches of ethyloxy units with a terminal iodide. Bisimidazole was



Scheme I. Synthesis of aromatic tri-iodide compound BTDI and bisimidazole.

prepared by the reaction of imidazole with the triethylene glycol ditosylate under a strong base, NaH, which particularly favors the reaction to give highly yield of desired products. $^1\text{H-NMR}$ spectra of BTDI and bisimidazole are shown in Figure 1. The aromatic protons of BTDI appeared at 8.92 ppm as a singlet and the aliphatic protons of ethyloxy unit at 3.28, 3.81, and 4.55 ppm as a triplet. The integral ratio was in a good agreement with the theoretical one and there were no impurity peaks, indicating successful preparation of the compound. In Figure 1(b) of $^1\text{H-NMR}$ spectrum of bisimidazole, the aromatic protons of imidazole ring are shown at 6.96, 7.04, and 7.52 ppm and the aliphatic protons of ethyloxy unit at 3.52 and 4.08 ppm.

We monitored formation of the imidazolium salt by curing reaction of BTDI and bisimidazole using a FT-IR measurement as shown in Figure 2. BTDI and bisimidazole were

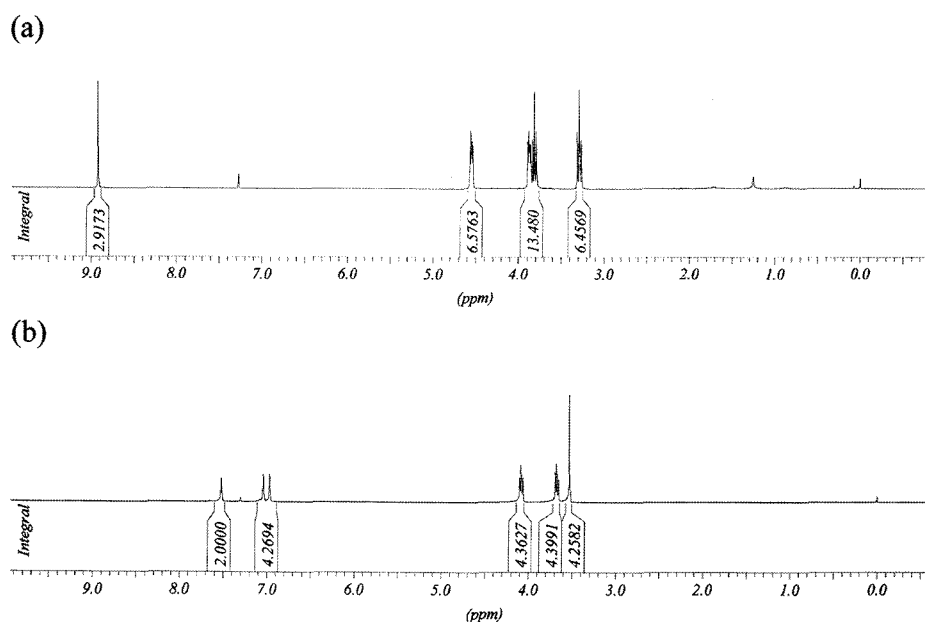


Figure 1. $^1\text{H-NMR}$ spectra of (a) BTDI and (b) bisimidazole.

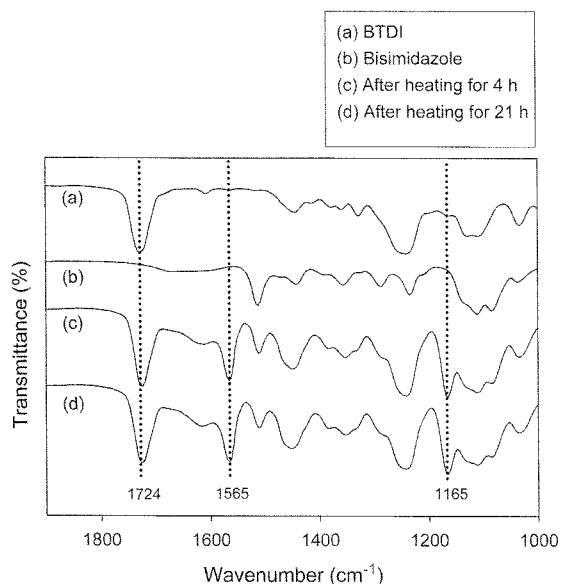
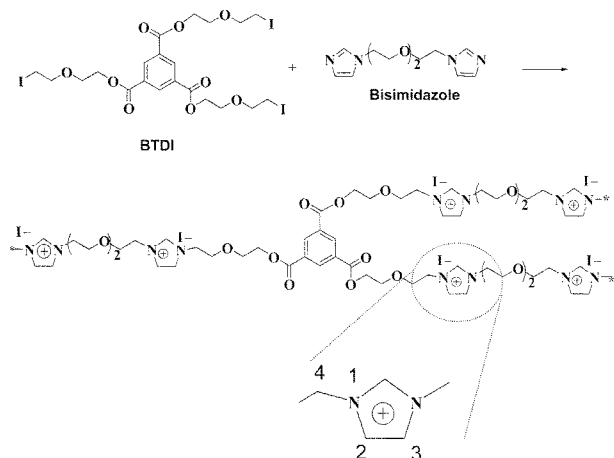


Figure 2. FT-IR spectra of (a) BTDI, (b) bisimidazole, (c) mixture of bisimidazole and BTDI heated at 100 °C for 4 h, and (d) mixture of bisimidazole and BTDI heated at 100 °C for 21 h.

mixed together at a mixing ratio of 2/3 (mol/mol). The mixture was coated on NaCl crystal window for IR measurement and was heated at 100 °C in order to induce curing reaction. The strong stretching vibration band at 1724 cm⁻¹ due to the carbonyl group in BTDI was almost intact during the curing process at 100 °C. When the mixture was heated for 4 h at 100 °C, new strong peaks appeared at 1565 and 1165 cm⁻¹. The new peak at 1565 cm⁻¹ was possibly due to the stretching vibration of N1-C2-C3 of the imidazolium salt (Scheme II).¹³ The peak at 1165 cm⁻¹ was resulted from the asymmetric vibration of N1-C4, which formed by alkylation of imidazole ring.¹³ It is noteworthy that the intensity of the two peaks changed not much after 4 h as can be seen in Figures 2(c) and (d). This indicated that the curing was



Scheme II. Preparation of poly(imidazolium iodide).

almost done at 100 °C for 4 h.

Precursors of the ionic gel polymer electrolytes were prepared by dissolving the gelating monomers (BTDI and bisimidazole) into the ionic liquid (LiI and I₂ dissolved in PMII). The resulting viscous mixture was injected in DSSC device through a syringe and allowed to permeate into the nanopores of TiO₂. To obtain a solidified ionic gel polymer electrolyte the cell was then cured at 100 °C for 4-5 h, which was dependent upon the monomer concentration. At the temperature lower than 100 °C, we failed to obtain a firm ionic gel polymer electrolyte. As shown in Scheme II, BTDI and bisimidazole were crosslinked together to form a network structure of poly(imidazolium iodide) by heating and made the ionic liquid a gel state, which was a quasi-solid state. As low as 30 wt% of the monomers (BTDI and bisimidazole) concentration in the electrolytes was found to be enough to form a gel type electrolyte. We failed to form a stable gel with 20 wt% of the monomer concentration. It should be noted that in our approach crosslinking was carried out after the liquid electrolytes were injected in the cell and permeated into the nanoporous TiO₂. Such *in situ* crosslinking is important to allow the gel polymer electrolytes to make a good interfacial contact with the nanopores in TiO₂ electrodes, which may decrease the interfacial resistance.

The gel polymer electrolytes have much better stability and very little leakage problem when compared with the liquid electrolyte. However, ionic conductivity was somewhat negatively affected by such gelation as shown in Figure 3. The ionic conductivity of the gel polymer electrolyte with 30 wt% of the monomer concentration (Figure 2(b)) was measured to be 2.92 × 10⁻⁴ S/cm at 30 °C, while the pristine ionic liquid electrolyte (i.e. without monomers) showed 6.27 × 10⁻³ S/cm, which was about one order of magnitude

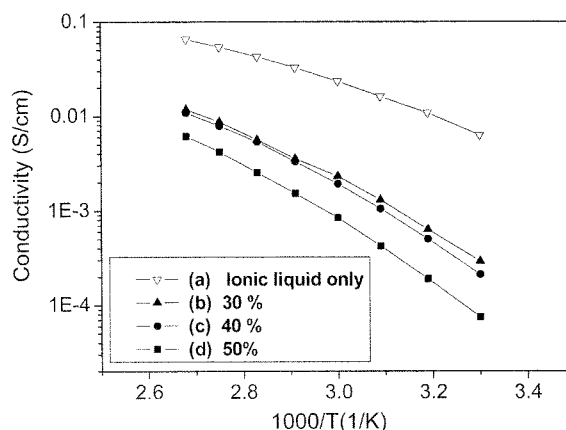


Figure 3. Ionic conductivity of the ionic polymer electrolytes with a different concentration of the monomers of poly(imidazolium iodide) as a function of temperature. The concentration of the monomers (BTDI and bisimidazole) was adjusted from 30 to 50 wt% in the ionic polymer electrolytes. For comparison ionic conductivity of the pristine ionic liquid was also presented.

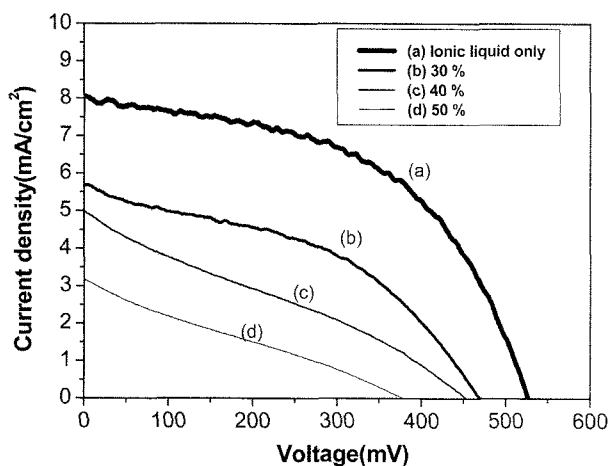


Figure 4. Photocurrent density (J) - voltage (V) curves of DSSCs based on the ionic polymer electrolytes with a different concentration of the monomers of poly(imidazolium iodide). The concentration of the monomers (BTDI and bisimidazole) was adjusted from 30 to 50 wt% in the ionic polymer electrolytes. The measurements were taken under AM 1.5 simulated sun light (100 mW/cm^2). (a) for ionic liquid only, $J_{sc} = 8.06 \text{ mAcm}^{-2}$, $V_{oc} = 527 \text{ mV}$, fill factor (FF) = 0.51, $\eta = 2.27\%$; (b) for 30 wt% monomer concentration, $J_{sc} = 5.69 \text{ mAcm}^{-2}$, $V_{oc} = 474 \text{ mV}$, FF = 0.43, power conversion efficiency (η) = 1.15%; (c) for 40 wt% monomer concentration, $J_{sc} = 4.99 \text{ mAcm}^{-2}$, $V_{oc} = 452 \text{ mV}$, FF = 0.28, $\eta = 0.36\%$; (d) for 50 wt% monomer concentration, $J_{sc} = 3.12 \text{ mAcm}^{-2}$, $V_{oc} = 373 \text{ mV}$, FF = 0.25, $\eta = 0.32\%$.

higher value than that of the gel polymer electrolyte. At higher monomer concentration, the ionic conductivity decreased more due to lower mobility of the ionic carriers in more densely crosslinked network. It is noteworthy that at higher temperature the gap in ionic conductivity decreased largely. For example, at 100°C the pristine ionic liquid electrolyte showed $6.54 \times 10^{-2} \text{ S/cm}$, which was only 5 times larger than that of the gel electrolyte derived from the precursor with 30 wt% monomer concentration.

Figure 4 shows the I-V curves of DSSCs based on the ionic gel electrolytes as well as the ionic liquid electrolyte. Like ionic conductivity, the characteristics of DSSCs using the gel electrolytes were somewhat deteriorated when compared to the ionic liquid electrolytes. For example, an open circuit voltage and a short circuit current density of DSSCs based on the gel electrolyte with 30 wt% of the monomer concentration were 474 mV and 5.69 mA/cm^2 , respectively,

while 527 mV and 8.06 mA/cm^2 for the ionic liquid electrolytes. The DSSCs based on the gel polymer electrolyte achieved as high as 1.15% of the power conversion efficiency, which was about half of the efficiency obtained by DSSC based on the ionic liquid electrolytes as shown in Figure 4.

Conclusions

In conclusion, we successfully demonstrated dye sensitized solar cells based on a stable ionic gel polymer electrolytes prepared by *in situ* crosslinking of aromatic triiodide compound and bisimidazole in ionic liquid. The resulting ionic gel polymer electrolytes were a quasi-solid state and hence showed no leakage problem in the cells. To enhance ionic conductivity and performance in the DSSCs of the gel polymer electrolytes are remaining tasks to be solved in the future.

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