COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Quasi-solid dye sensitised solar cells filled with phase-separated chemically cross-linked ionic gels

Shinji Murai,*[a] Satoshi Mikoshiba,[a] Hiroyasu Sumino,[a] Takashi Kato[b] and Shuzi Hayase[b]
[a] *Komukai-Toshiba-cho, Saiwai-ku, Kawasaki 212-8582, Japan. E-mail: shinji.murai@toshiba.co.jpc;*
Fax: 044-520-1286; Tel: 044-549-2120
[b] *2–4, Hibikino, Wakamatsu-ku, Kitakyushu 808-0196, Japan. E-mail: hayase@life.kyutech.ac.jp;*
Fax: 093-695-6005; Tel: 093-695-6044

Received (in Cambridge, UK) 12th March 2003, Accepted 23rd April 2003
First published as an Advance Article on the web 29th May 2003

Quasi-solid dye sensitised solar cells were prepared by gelling ionic liquid electrolytes with phase-separated chemically cross-linked gels which make it possible to solidify DSSC without losing the performance of the parent DSSC.

Dye sensitised solar cells (DSSCs) have been reported to exhibit high light–current conversion efficiencies reaching 10% and are one of the promising candidates for the next generation of solar cells.[1] DSSCs contain liquid electrolytes diluted with volatile organic solvents. Because of their high volatilities, solvent losses occur during long-term operations, resulting in lowered DSSC performances.[2] Solidification of liquid electrolytes with gelators is one of the solutions.[3–12] We aimed at solidifying non-volatile ionic liquids with chemically cross-linked gelators. Ionic liquids have high conductivities as well as non-volatile properties.[13,14] They have been solidified with physically cross-linked gelators so far.[9–12] There was no report on chemically cross-linked gel electrolyte precursors containing redox species (I^-/I_3^-). Since conventional gelators do not work in the presence of redox species, previously reported chemically cross-linked gel electrolytes were prepared by impregnating the redox species into gels once prepared.[15,16]

Solidification of electrolytes with gelators frequently decreases the device performance because diffusions of ionic species are retarded by polymer backbones. Gelators also increase interfacial resistances between gel electrolytes and electrodes.[17–20] We now report that micro-phase separated gel electrolytes do not retard the ionic motions and maintain the photo-voltaic performance after the solidification.

How to make good contacts between nano-porous titanium dioxide and (quasi) solid electrolytes is a crucial problem. Physically cross-linked gel electrolytes usually contain high molecular weight polymers as gelators and they become fluids at high temperatures. However, except for one example,[9,10] the initial viscosity for the gel electrolyte at elevated temperatures is still high. Therefore it is hard to impregnate the gel electrolytes into the pores in TiO_2 layers directly. Almost all quasi-solid dye sensitised solar cells were prepared by repeating the following process: coating of diluted electrolyte precursors on the porous titanium layers and evaporation of the diluents. We used a new process to fill the pores. Our gel electrolytes contain polyvinylpyridine (PVP) and organic halides as gelators, and imidazolium iodides (ionic liquids, Table 1). Since PVPs are oligomers, initial viscosities for our gel electrolyte precursors are not high and it is possible to impregnate the precursors directly into nano-porous titanium dioxide layers. When the cell is heated, gelators are cross-linked through chemical bonding. Gelations occur directly in the cells. The process is simple and realizes good physical contacts between porous titanium dioxide layers and gel electrolytes.

The second problem to be solved is the diffusion retardation caused by interactions between gelator backbones and ionic species, I_3^-. We found that one gelator exhibited excellent properties and this was caused by micro-phase separations during gelation.

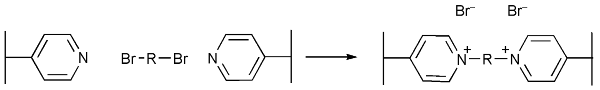
cis-Di(thiocyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II)(N3) and TiO_2 paste (Ti-Nanoxide D) were purchased from Solaronix SA. Fluorine-doped SnO_2 layered glass plates (7–8 Ω $square^{-1}$)(SnO_2/F) were obtained from Nippon Sheet Glass Co. Ltd. Compositions for gel electrolyte precursors are summarized in Table 1, where GP stands for gel electrolyte precursors and G stands for gel electrolytes after solidification. PVP (Mw 60,000), alkyl dihalide and tetra(bromomethyl)benzene were purchased from Aldrich Corporation. Ti-Nanoxide D paste was coated on SnO_2/F layered glasses by using a metal mask (30 micron) and baked at 450 °C for 30 min. TiO_2 layers with 6 micron thickness were obtained by repeating the process twice. We did not aim to obtain best performance but to compare the PV performances accurately. Therefore, we chose the thin TiO_2 thickness for the reproducibility. The TiO_2 layers were immersed in N3 dye solutions in ethanol (0.1%) at room temperature over night. After the TiO_2 electrodes were rinsed with ethanol, they were dried at room temperature in the dark. Pt sputtered SnO_2/F layered glass substrates were employed as counter electrodes. A plastic sheet (Surlyn, Dupont. Co. Ltd., 40 micron) was inserted between TiO_2 electrodes and counter electrodes as the spacer. Gel electrolyte precursors were injected in the cell at room temperature. Then the cells were heated at 80 °C for 5 min. The gelation is brought about by reacting PVP with cross-linkers to make chemically cross-linked ionomer structures (Scheme 1). Finally, the cells are sealed with epoxy resins. The active cell area is 1 cm^2.

Interfacial resistances were monitored by the method described in the previous literature.[18,19] The symmetrical cells sandwiched with two sputtered Pt electrodes fabricated on SnO_2/F layered glass substrates, were used for the measurement. Interfacial resistances between Pt sputtered electrodes

Table 1 Compositions for gel electrolyte precursors

	Gelator				
	Backbone oligomer		Crosslinker		Electrolytes
Abbreviation	Structure	Parts	Structure	Parts	Parts
GP1	PVP	4	C3Cl2	2.2	100
GP2	PVP	4	C4Cl2	2.4	100
GP3	PVP	4	C6Br2	4.6	100
GP4	PVP	4	C10Br2	5.7	100
GP5	PVP	2	B4Br	2.2	100
RF	non		non		100

Electrolyte: methylpropylimidazolium iodide (MePrImI) containing 5% of water, I_2: 300 mM, PVP: polyvinylpyridine; C3Cl2: dichloropropane; C4Cl2: dichlorobutane C6Br2: dibromohexane; C10Br2: dibromedecane; B4Br: tetra(bromomethyl)benzene.



Scheme 1

DOI: 10.1039/b302793g

Table 2 PV Performances for DSSCs filled with gel electrolytes and gel electrolyte properties

	PV Performance		Electrolyte properties		
Abbreviation	V_{oc}/mV	J_{sc}/mA cm^{-2}	C.T. resistance/ Ω cm^{-2}	Diffusion constant/cm^2 s^{-1}	Gel
G1	580	4.1	5.5	1.8	Transparent
G2	580	4.2	5.6	1.7	Transparent
G3	570	4.1	5.9	1.4	Transparent
G4	580	4.8	6.3	1.3	Transparent
G5	540	6.5	1.8	2.8	Turbid
RF	500	6.3	0.8	3	

G1: Gel electrolyte solidified from GP1; V_{oc}: open current voltage; J_{sc}: short circuit current; C.T. resistance: charge transfer resistance; Pt/electrolyte/Pt cell area: 1 cm^2; AM1.5, 100 mW cm^{-2}; TiO_2 thickness 6 μm.

and gel electrolytes were estimated by using a Cole–Cole plot. Impedance spectra were recorded over frequency ranges from 0.01 Hz to 100 kHz. Photoelectrochemical measurements were performed using solar simulator (WXS-R50S-1.5, Maki Manufacturing Co. Ltd.) furnished with a xenon lamp (AM 1.5, 100 mW cm^{-2}). The light intensity was monitored with a poly-silicon illuminometer standardized by the Japan Quality Assurance Organization.

Gel electrolyte precursors (GP1–GP5) were homogeneous liquids initially and were injected into the cell without difficulty. Gel electrolyte precursors containing alkyldihalides (GP1–GP4) provided transparent gels visually, after they were heated. However, GP5 provided turbid gels. Apparently phase separated gels formed during gelation in the cells. The inhomogeneity was supported by the results that when laser beams were passed through G5 gels, an increase in the laser beam diameter due to diffraction was observed. The phenomena were not observed for other gels. Table 2 summarizes the PV performances and gel electrolyte properties. V_{oc} was 500 mV for DSSCs containing no gelators. After gelation, V_{oc} increased from 500 to 540 and 580 mV. The gelator contains PVP which increases V_{oc}.[21] Large differences were not observed among different cross-linkers in terms of V_{oc}. J_{sc} for DSSCs containing RF was 6.3 mA cm^{-2}. Large decreases in J_{sc} were observed for DSSCs containing alkyldihalides (GP1–GP4) from 6.3 to 4.8–4.1 mA cm^{-2}. However, J_{sc} for DSSC containing G5 was almost the same as that for RF electrolyte.

Charge transfer resistances between gel electrolytes and Pt electrodes were 0.8 Ω cm^{-2} in the case of RF electrolytes. The resistance increased a little to 1.8 Ω cm^{-2} for G5 electrolyte. Large increases in the resistance were observed for other gel electrolytes (G1–G4). Apparent diffusion constants for G5 electrolyte were almost the same as those for RF. On the contrary, the diffusion constants for other gels decreased to a half of those for RF and G5. Apparently, performances for G5 gel were different from those for other gels containing alkyldihalides (G1–G4). We also observed phase-separations when bis(bromomethyl)benzene was used for cross-linkers. The PV performance was almost the same as that for G5. The data are not shown in Table 2, because the cell preparation conditions were different from those in Table 2. Whether the cross-linker has two or four halides is not crucial. The conductivity of gel electrolytes decreased only from 10 to 9 mS cm^{-1} and the decrease seemed to be saturated when the amount of cross-linker B4Br increased from 2 to 10%. The conductivity decreased largely from 8 to 1 mS cm^{-1} when the amount of C6Br2 increased from 4 to 10%. These experimental results are explained well as follows. In the homogeneous gels (G1–G4), I_3^- species interact with cations in gelator backbones, which retard ionic diffusions. However, in the case of phase-separated gel (G5), I_3^- species can move around like in liquid electrolytes because gelator backbones are somehow phase-separated from the fluid phases.

We observed the fact that the charge transfer resistance between Pt electrodes and electrolytes decreased from 5.4 Ω cm^{-2} to 3.7 Ω cm^{-2} after the Pt electrode was soaked with B4Br. We suspect that B4Br bonded on Pt electrodes facilitates reduction of I_2 on Pt. Further investigation is in progress.

In conclusion, we found that DSSCs containing ionic liquids were solidified with chemically cross-linked ionomer gelators. Phase-separated gels showed excellent performances after gelation. The gel electrolyte precursors were homogeneous and inserted into cells without difficulty. This assured the physical contacts between gel electrolytes and porous TiO_2 layers. This made it possible to solidify DSSCs without losing the initial performances.

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (417) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government (to S. Hayase and T. Kato).

Notes and references

1 A. Hagffeldt and M. Gratzel, *Chem. Rev.*, 1995, **95**, 49.
2 N. Papageorgiou, W. Maier and M. Gratzel, *J. Electrochem. Soc.*, 1997, **144**, 876.
3 A. F. Nogueira and M. A. D. Paoli, *Sol. Energy Mater. Sol. Cells*, 2000, **61**, 127.
4 S. Yanagida, S. Kambe, W. Kubo, K. Murakoshi, T. Wada and T. Kitamura, *Z. Phys. Chem.*, 1999, **Bd212**, S.38.
5 K. Tennakone, G. K. R. Senadeera, V. P. S. Perera, I. R. M. Kottegoda and L. A. A. De Silra, *Chem. Mater.*, 1999, **11**, 2474.
6 E. Stathatos, P. Lianos, U. L-Stangar and B. Orel, *Adv. Mater.*, 2002, **14**, 354.
7 Y. Ren, Z. Zhang, S. Fang, M. Yang and S. Cai, *Sol. Energy Mater. Sol. Cells*, 2002, **71**, 253.
8 O. A. Ileperuma, M. A. K. L. Disssanayake and S. Somasundaram, *Electrochim. Acta*, 2002, **47**, 2801.
9 W. Kubo, K. Murakoshi, T. Kitamura, S. Yoshida, M. Haruki, K. Hanabusa, H. Shirai, Y. Wada and S. Yanagida, *J. Phys. Chem. B*, 2001, **105**, 12809.
10 W. Kubo, T. Kitamura, K. Hanabusa, Y. Wada and S. Yanagida, *Chem. Commun.*, 2002, 374.
11 P. Wang, S. M. Zakeeruddin, I. Exnar and M. Graetzel, *Chem. Commun.*, 2002, 2972.
12 P. Wang, S. M. Zakeeruddin, P. Comte, I. Exnar and M. Graetzel, *J. Am. Chem. Soc.*, 2003, **125**, 1166.
13 B. O'Regan and D. T. Schwartz, *J. Appl. Phys.*, 1996, **80**, 4749.
14 B. O'Regan and D. T. Schwartz, *Chem. Mater.*, 1995, **7**, 1349.
15 M. Matsumoto, H. Miyazaki, K. Matshushiro, Y. Kamishiro and Y. Takaoka, *Solid State Ionics*, 1996, **89**, 263.
16 M. Matsumoto, H. Miyazaki and Y. Kamishiro, *Nippon Kagaku Kaishi*, 1997, 484.
17 M. Watanabe, K. Sanui, N. Ogata, T. Kobayashi and Z. Ohtaki, *J. Appl. Phys.*, 1985, **57**, 123.
18 M. Kono, E. Hayashi and M. Watanabe, *J. Electrochem. Soc.*, 1999, **146**, 1626.
19 M. Kono, E. Hayashi, M. Nishimura and M. Watamabe, *J. Electrochem.Soc.*, 2000, **147**, 2517.
20 M. Kono, M. Nishimura and E. Ishiko, *J. Power Sources*, 1999, **81–82**, 748.
21 S. Y. Huang, G. Schlichthorl, A. J. Nozik, M. Gratzel and A. J. Frank, *J. Phys. Chem. B*, 1997, **101**, 2576.