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Latent gel electrolyte precursors for quasi-solid dye sensitized solar cells

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New latent chemically-cross-linked gel electrolyte precursors for quasi-solid dye sensitized solar cells (QDSC) are reported. The gel electrolyte precursors consist of nano-particles and dicarboxylic acids as the latent gelators. The viscosity of the precursor is low at first and does not increase during storage at room temperature. However, when the precursor is baked at 80 °C, it solidifies immediately. Photo-voltaic performance is maintained after solidification.

Dye sensitized solar cells (DSC) contain volatile liquid electrolytes.[1] Therefore, achieving solidification is one of the crucial research areas; all-solid DSCs have been reported previously.[2–10] We have taken another approach, namely, solidification with gel electrolytes,[11–27] focussing on chemically cross-linked gel electrolytes (CCGE) containing ionic liquids to decrease the volatility of the electrolytes.[17–27] CCGEs have an advantage over physically cross-linked gel electrolytes in terms of their heat-resistant properties. However, preparation of CCGEs is very difficult because iodine species inhibit vinyl polymerization and epoxide ring-opening polymerization, which have been commonly used for gelations. We have already reported gel electrolyte precursors (Gel-Pre) consisting of polyvinylpyridine (PVP) and 1,2,4,5-tetrakis-(bromomethyl)benzene (B4Br) as the gelator.[24–27] Gel-Pre with low viscosity was injected between a porous TiO_2 electrode and counter electrode at room temperature. The cell was then heated at 80 °C to achieve gelation in the cell. By using this method, contacts between quasi-solid electrolyte and TiO_2 particle in porous TiO_2 layers were improved.[24–27] However, there was a problem to be solved: immediately after the PVP, B4Br and liquid electrolytes were mixed, the viscosity started to increase. This made it difficult to fabricate large cells, for which a long impregnation time is required.

We therefore propose a new concept for Gel-Pre, namely "latent gel electrolyte precursors (L-Gel-Pre)", in which the gelation abilities of the gelators are hidden at room temperature, and the solidification occurs suddenly at a certain higher temperature.

Compositions of gel electrolyte precursors are summarized in Table 1. Ti-Nanoxide D paste (Solaronix SA) was coated on SnO_2/F layered glasses (30 ohm per square, Nippon Sheet Glass Co. Ltd.). The substrates were baked at 450 °C to fabricate 9 micron thick TiO_2 layers. The substrates were immersed in *cis*-di(thicyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) (Kojima Kagaku) solution in ethanol (0.1%). Pt-sputtered SnO_2/F layered glass substrates were employed as counter electrodes. A plastic sheet (HIMILAN, Mitsui-Dupont Co. Ltd., 50 micron) was inserted between the TiO_2 electrode and the counter electrode as a spacer. Gel-Pre was injected in the cell at room temperature, and the cells were heated at 80 °C for 1 min. The cell area was 0.25 cm^2. Photo-electrochemical measurements were performed using a solar simulator (YSS-50A, Yamashita Denso Co. Ltd., AM 1.5, 100 mW cm^{-2}).

Table 1 Summary of gel electrolyte precursors and their compositions

Abbreviation[a]	Electrolyte TS3[b]	Nano-particle[c]	Dicarboxylic acid	Gelation?
Pregel-C6-300	100	3	3	No[d]
L-Gel-Pre-C12-300	100	3	3	Yes
L-Gel-Pre-C16-300	100	3	3	Yes

[a] C6: $HOOC(CH_2)_4COOH$, C12: $HOOC(CH_2)_{10}COOH$, C16: $HOOC(CH_2)_{14}COOH$. [b] Electrolyte (TS3): MePrImI (containing 5% water), I_2 300 mM, *t*-BuPy 580 mM, LiI 500 mM. [c] AEROSIL 300 (Nippon Aerosil). [d] After a swift reaction, precipitation occurred.

In our L-Gel-Pre system, nano-particles and hexadecanedioic acid (C16) were dispersed in ionic liquid type electrolytes. L-Gel-Pre did not show any viscosity increase for at least a couple of days, but when it was heated at 80 °C, solidification occurred immediately. The selection of nano-particles and dicarboxylic acids to realize latent properties is discussed in the following section.

Gratzel and co-workers have reported gel electrolytes consisting of ionic liquids and silica nano-particles.[20,21] Usui, Yanagida and co-workers have also reported gel electrolytes containing ionic liquids and nano-particles.[22] Kim and his co-workers have recently reported composite polymer electrolytes containing nano-particles.[23] These nano-particles act as physically cross-linked gelators. These gel electrolytes are injected into porous TiO_2 layers by coating before cell preparation or by injecting electrolytes melted at higher temperature, because they are solid at room temperature. In our system, nano-particles are added to provide only cross-linking points (Fig. 1). Therefore, the amount and variety of nano-particles have to be selected in order not to increase viscosity of

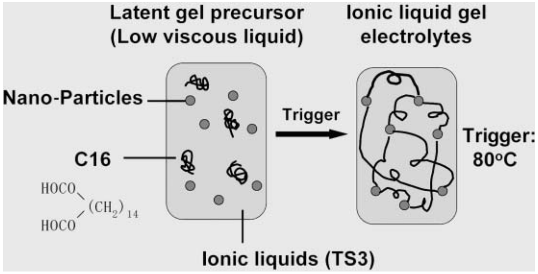

Fig. 1 Mechanism for solidification of L-Gel-Pre.

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Gel-Pre at room temperature. The following nano-particles were dispersed in TS3 electrolytes and increases in the viscosity were examined. Hydrophilic SiO_2 particles: AEROSIL 50 (diameter 30 nm, 10 wt% needed to lose fluidity), 300 (7 nm, 5 wt%), 200 (12 nm, 5%). Hydrophobic SiO_2 particles: Aerosil R805 (12 nm, 3 wt%). Hydrophilic TiO_2 particles: P25 (21 nm, 14wt%). Hydrophobic TiO_2 particles: T805 (21 nm, 6 wt%). The amount of the nano-particles needed to lose fluidity decreased with a decrease in the particle size. Increases in viscosities for hydrophobic nano-particles were much more remarkable than those for hydrophilic nano-particles. We selected AEROSIL 300 because this did not increase electrolyte viscosities up to 3 wt%, and was dispersed well in ionic liquids.

Three dicarboxylic acids were selected to compare their latent properties. In case of C6, with a short alkyl chain, immediately after AEROSIL 300 nano-particles and C6 were added to the electrolytes, precipitation occurred as a result of reaction. However, in the case of L-Gel-Pre-C10-300 and L-Gel-Pre-C16-300, the reaction did not occur at room temperature when C10 or C16 and 300 nano-particles were mixed with TS3 electrolyte. Fig. 2 shows the viscosity change. In case of the TS3-PVP-B4Br Gel-Pre previously reported by us,[24–27] the viscosity increased gradually even at room temperature.

When L-Gel-Pre-C16-300 was heated to 80 °C, solidification occurred swiftly. The gel did not return to a liquid state even after it was heated at 100 °C. The latent mechanism is associated with a thermal phase transition of C16 in ionic liquid electrolytes. The (reversible) phase transition of C16 in TS3 was observed at around 80 °C on heating and cooling. However, the phase transition was not observed for C6 in TS3 electrolytes, suggesting that C6 is dissolves in ionic liquids even at room temperature. The melting point for C16 alone was 110 °C, which is slightly higher than the phase transition temperature for C16 in ionic liquids. Therefore, C16 would be present as phase-separated particles, slightly swelled by ionic liquids at room temperature. Therefore, nano-particle and phase-separated C16 did not react. At 80 °C, the phase transition of C16 occurs and C16 becomes soluble in ionic liquids. The dissolved C16 can react with nano-particle surfaces; nano-particles play the role of cross-linking sites and C16 acts as a latent cross-linkers (Fig. 1).

Fig. 3 shows photocurrent–voltage curves before and after solidification. Before gelation, V_{oc}, J_{sc}, the fill factor (ff) and the energy conversion efficiency were 0.65 V, 12.40 mA cm^{-2}, 0.63 and 5.03%, respectively. After gelation, they were 0.67 V, 13.00 mA cm^{-2}, 0.66 and 5.74%, respectively. This clearly shows that even after solidification, the photo-voltaic performance did not decrease. The slight increase in the photo-conversion efficiencies after gelation may be associated with the added dicarboxylic acid. We have already reported that surface modification of TiO_2 particles with carboxylic acids decreases interfacial resistances in TiO_2 layers and increases the photo-energy conversion efficiencies.[28] In addition, enhanced electron exchange mechanisms between iodine and iodide ion organized on the surfaces of nano-particles, reported by Usui and co-workers, may be associated with the improvement of cell performance.[22] Our best result obtained recently was 0.66 (V_{oc}), 16.5 mA cm^{-2} (J_{sc}), 0.63 (ff) and 6.8% (efficiency).

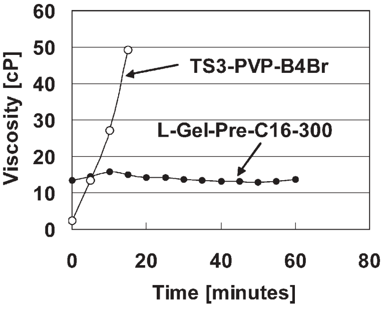

Fig. 2 Viscosity *vs.* time at room temperature for TS3-PVP-B4Br: PVP 3 wt%, B4Br (1,2,4,5-tetrabromomethylbenzene) 3 wt% in TS3 electrolyte.

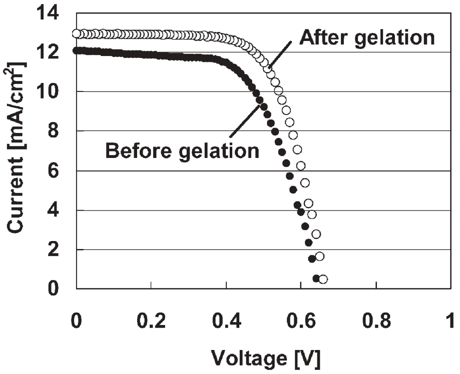

Fig. 3 Photocurrent *vs.* voltage before gelation: TS3. After gelation: L-Gel-Pre-C16-300 gel.

In conclusion, we have proposed a new type of gel electrolyte precursor, namely, latent gel electrolyte precursors. Two contrasting properties; the long shelf life of Gel-Pre and swift gelation at an elevated temperature, were fulfilled by use of phase-separated dicarboxylic acids having long alkyl chains. This contributes to the fabrication of large scale quasi-solid dye sensitized solar cells.

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Notes and references

1 A. Hagffeldt and M. Gratzel, *Chem. Rev.*, 1995, **95**, 49.
2 K. Tennakone, J. Bandara, P. K. M. Bandaranayake, G. R. A. Kumara and A. Konno, *Jpn. J. Appl. Phys., Part 2*, 2001, **40**, L732.
3 G. R. A. Kumara, A. Konno and K. Tennakone, *Chem. Lett.*, 2001, 180.
4 T. Taguchi, X.-T. Zhang, I. Sutanto, K. Tokuhiro, T. N. Rao, H. Watanabe, T. Nakamori, M. Uragami and A. Fujishima, *Chem. Commun.*, 2003, 2480.
5 K. Tennakone, G. R. R. A. Kumara, I. R. M. Kottegoda, V. P. S. Perera and P. S. R. S. Weerasundara, *J. Photochem. Photobiol., A*, 1998, **117**, 137.
6 B. O'Regan and D. T. Schwartz, *J. Appl. Phys.*, 1996, **80**, 4749.
7 D. Gebeyehu, C. J. Brabec, N. S. Sariciftci, D. Vangeneugden, R. Kiebooms, D. Vanderzande, F. Keinberger and H. Schindler, *Synth. Met.*, 2002, **125**, 279.
8 B. O'Regan and D. T. Schwartz, *Chem. Mater.*, 1995, **7**, 1349.
9 U. Bath, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer and M. Graetzel, *Nature*, 1998, **395**, 583.

10 K. Tennakone, G. K. R. Senadeera, D. B. R. A. De Silva and I. R. M. Kottegoda, *Appl.Phys.Lett.*, 2000, **70**, 2367.
11 S. Yanagida, S. Kambe, W. Kubo, K. Murakoshi, T. Wada and T. Kitamura, *Z. Phys. Chem. (Munich)*, 1999, **Bd212**, S.38.
12 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.
13 E. Stathatos, P. Lianos, U. Lavrencic-Stangar and B. Orel, *Adv. Mater.*, 2002, **14**, 354.
14 Y. Ren, Z. Zhang, S. Fang, M. Yang and S. Cai, *Sol. Energy Mater. Sol. Cells*, 2002, **71**, 253.
15 O. A. Ileperuma, M. A. K. L. Disssanayake and S. Somasundaram, *Electrochim. Acta*, 2002, **47**, 2801.
16 P. Wang, S. M. Zakeeruddin, J. Moser, M. K. Nazeeruddin, T. Sekiguchi and M. Gratzel, *Nat. Mater.*, 2003, **2**, 402.
17 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.
18 W. Kubo, T. Kitamura, K. Hanabusa, Y. Wada and S. Yanagida, *Chem. Commun.*, 2002, 374.
19 P. Wang, S. M. Zakeeruddin, I. Exnar and M. Graetzel, *Chem. Commun.*, 2002, 2972.
20 P. Wang, S. M. Zakeeruddin, P. Comte, I. Exnar and M. Graetzel, *J. Am. Chem. Soc.*, 2003, **125**, 1166.
21 E. Stathatos, P. Lianos, S. M. Zakeeruddin, P. Liska and M. Gratzel, *Chem. Mater.*, 2003, **15**, 1825.
22 H. Usui, H. Matsui, N. Tanabe and S. Yanagida, *J. Photochem. Photobiol., A:*, 2004, **164**, 97.
23 J. H. Kim, M.-S. Kang, Y. J. Kim, J. Won, N.-G. Park and Y. S. Kang, *Chem. Commun.*, 2004, 1662.
24 S. Murai, S. Mikoshiba, H. Sumino, T. Kato and S. Hayase, *Chem. Commun.*, 2003, 1534.
25 S. Mikoshiba, S. Murai, H. Sumino and S. Hayase, *Chem. Lett.*, 2002, 1156.
26 S. Mikoshiba, S. Murai, H. Sumino and S. Hayase, *Chem. Lett.*, 2002, 918.
27 Y. Shibata, T. Kato, T. Kado, R. Shiratuchi, W. Takashima, K. Kaneto and S. Hayase, *Chem. Commun.*, 2003, 2730.
28 S. Sakaguchi, H. Ueki, T. Kato, T. Kado, R. Shiratuchi, W. Takashima, K. Kaneto and S. Hayase, *J. Photochem. Photobiol., A*, 2004, **164**, 117.