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Quasi-solid-state dye-sensitized solar cells using room temperature molten salts and a low molecular weight gelator

Wataru Kubo,[a] Takayuki Kitamura,[a] Kenji Hanabusa,[b] Yuji Wada[a] and Shozo Yanagida*[a]

[a] *Material and Life Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka Suita 565-0871, Japan. E-mail: yanagida@chem.eng.osaka-u.ac.jp*

[b] *Graduate School of Science and Technology, Shinshu University Ueda 386-8567, Japan*

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A dye-sensitized solar cell fabricated using the room temperature molten salt, 1-hexyl-3-methylimidazolium iodide, iodine and a low molecular weight gelator as a quasi-solid-state electrolyte showed a 5.0% light-to-electricity conversion efficiency under AM 1.5 irradiation, and high-temperature stability.

Dye-sensitized solar cells constructed using dye molecules, nanocrystalline metal oxides and liquid electrolytes have the attractive features of high photon-to-current conversion efficiency and low production cost and energy.[1] The electrolyte used in these cells, that is usually composed of an I^-/I_3^- redox couple in organic solvent, was sealed between two conducting glass substrates. The disadvantages of using liquid electrolytes are less long-term stability, difficulty in robust sealing and leakage of electrolyte in case of breaking of the glass substrates. While several attempts were made to improve long-term stability using p-type semiconductors[2] or conducting organic materials[3,4] instead of a liquid electrolyte, the stability of the solid cells was not adequate for practical use. Recently, dye-sensitized solar cells using gel electrolytes showed comparable efficiencies to cells using liquid electrolytes[5–7] and excellent stability in long-term stability tests.[8] For outdoor use, however, the presence of organic solvents in the gel electrolytes will cause problems such as high-temperature instability and flammability.

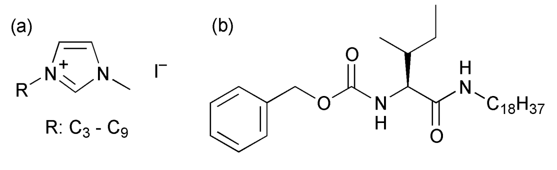
Currently, many chemically inert molten salts, which are of interest as electrolytes in electrochemistry because of their attractive features such as high conductivity, wide electrochemical window, non-volatility, thermal stability and non-flammability, are used as solvents for electrochemical experiments. Some papers reported the capability of room temperature molten salts as both iodide sources and solvents of electrolytes in solar cells.[9,10] However, the conversion efficiencies of the cells with molten salts are lower than those of the cells using a liquid electrolyte containing conventional organic solvent.

In a previous report, we described the importance of electron conduction in a concentrated I^-/I_3^- redox electrolyte caused by rather packed polyiodide species.[8] The charge in the I^-/I_3^- redox electrolyte was transported by electron conduction through iodide bond exchange. Here, we report on the fabrication, performance and high-temperature stability of quasi-solid-state dye-sensitized solar cells synthesised using neat room temperature molten salts, I_2 and a gelator. The molten salts used as high ionic strength iodide solutions should enhance the electron conduction in the electrolyte.

1-Alkyl-3-methylimidazolium iodides (Scheme 1a) were prepared by the quaternization reaction of 1-methylimidazole with an equimolar amount of the corresponding alkyl iodide (C_3–C_9) at 120 °C for 12 h in cyclohexane. The product was washed with diethyl ether to remove remains of the starting materials and dried under vacuum at 75 °C for 4 h, and was identified by ^1H NMR in $CDCl_3$. The gelator (Scheme 1b) was prepared as described elsewhere.[11]

Photoelectrochemical cells were fabricated as previously described.[8] Molten salt electrolytes (MEs) consisted of imidazolium iodides and 1/10 molarity of iodine without using any other solvents. A gelled molten salt electrolyte (GME) was prepared by adding 40 g L^{-1} of gelator to the chosen ME. As a reference, an organic solvent electrolyte (OE) was prepared using 0.6 M of 1,2-dimethyl-3-propylimidazolium iodide, 0.1 M of lithium iodide, 0.05 M of iodine and 0.5 M of 4-*tert*-butylpyridine dissolved in methoxyacetonitrile. A gelled organic solvent electrolyte (GOE) was again prepared by adding 40 g L^{-1} of gelator to the OE. Photoenergy conversion efficiencies were evaluated under AM 1.5 irradiation (from a solar simulator) adapted to the Japanese Industrial Standard for amorphous solar cells.[12] Each value for cell performance was taken as an average of at least 3 samples.

1-Alkyl-3-methylimidazolium iodides (alkyl chain: C_3–C_9) are viscous liquids. Viscosity of the molten salts increases with increasing alkyl chain length because of van der Waals forces.[13] As seen in Table 1, the conductivity of the molten salts decreases with increasing viscosity, since the diffusion of ions in a liquid depends on its viscosity. Photocurrent–voltage properties of the cells with imidazolium iodides are also listed in Table 1. The short circuit photocurrent density (J_{SC}) increased with increasing alkyl length up to C_7. Recently, an increase in the diffusion coefficient of an electron injected in a TiO_2 electrode (D_n) caused by multi-layer adsorption of imidazolium cations was observed.[14] Van der Waals forces of the alkyl chain would induce the aggregation of imidazolium cations, and adsorption of the aggregate could increase the J_{SC} with increasing D_n. Because the effect of D_n overcomes the decrease in conductivity (dark current of the cells decreases with increasing alkyl chain length), J_{SC} increased up to C_6 or C_7. The open circuit voltage (V_{OC}) also showed a maximum at C_7 because the quasi-Fermi level of the TiO_2 electrode rose with increasing J_{SC}. As a result, the electrolyte with 1-hexyl-3-methylimidazolium iodide gave the highest photoenergy



Scheme 1 Chemical structures of (a) 1-alkyl-3-methylimidazolium iodides and (b) gelator.

Table 1 Cell performance of the dye-sensitized solar cells with imidazolium iodides (ME) and their properties[a]

Imidazolium	$10^5\sigma$/ S cm^{-1}	Viscosity/ mPa s	V_{OC}/V	J_{SC}/mA cm^{-2}	*FF*	η (%)
C_3	80	865	0.593	5.99	0.593	2.11
C_4	49	963	0.602	6.56	0.615	2.43
C_5	37	1362	0.647	7.25	0.681	2.97
C_6	19	1439	0.670	7.36	0.661	3.26
C_7	15	1792	0.698	7.42	0.631	2.80
C_8	14	1976	0.687	6.65	0.615	2.80
C_9	8	2099	0.683	6.60	0.600	2.71

[a] Measured at 25 °C, average of at least 3 samples.

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conversion efficiency (η), and was used as the component of the GME.

Fig. 1 shows the photocurrent–voltage curves of the cells with the molten salt electrolyte, ME and GME under AM 1.5 irradiation. The V_{OC}, J_{SC}, fill factor (FF) and η of the cells are listed in Table 2. The curve obtained from the GME cell was similar to that of the ME cell. This result implies that the gelator establishes a three-dimensional network structure, without inhibition of charge transport,[8] even in a molten salt electrolyte as in organic electrolyte solutions. The conversion efficiency obtained from the GME cell was *ca.* 2/3 of the OE cell.

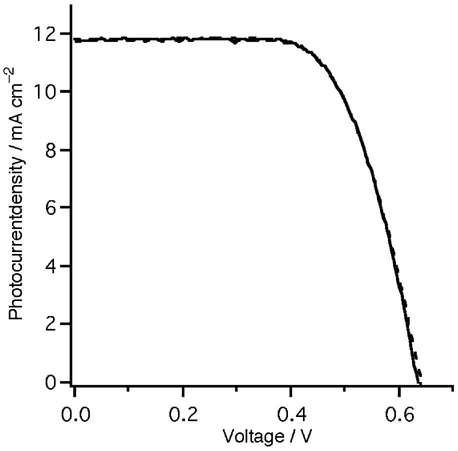

Fig. 1 Photocurrent–voltage curves of the cells with 1-hexyl-3-methylimidazolium iodide containing 8.7 wt% of I_2 under AM 1.5 irradiation; with (GME: solid curve) and without (ME: long dashed curve) 40 g L^{-1} of gelator.

Table 2 Photoelectrochemical performance of the dye-sensitized solar cells

Electrolyte	Area/cm^2	V_{OC}/V	J_{SC}/mA cm^{-2}	FF	η (%)
OE	0.242	0.718	16.6	0.666	7.92
GOE	0.242	0.746	14.5	0.679	7.37
ME	0.271	0.639	11.8	0.663	5.00
GME	0.267	0.635	11.8	0.669	5.01

The dry heat test on the cells, which were sealed with HIMILAN adhesive film and Torr Seal epoxy resin as described before,[8] was carried out. The cells were stored at 85 °C for 1000 h,[15] and their photoconversion efficiency was measured twice a week at 25 °C. The efficiency of the OE and GOE cells decreased immediately due to solvent evaporation, but the ME cells kept 70% of their initial efficiency because there are no volatile solvents. The efficiency of the GME cell did not decrease at all (Fig. 2).

Thus a high-temperature stabilized and non-flammable electrolyte composed of a room temperature molten salt and a gelator provides the practical efficiency and stability of a dye-sensitized solar cell.

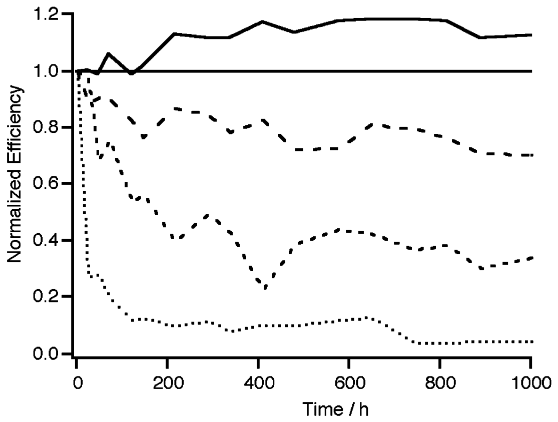

Fig. 2 Time-course change under dry heat test of the normalized photoconversion efficiency of the solar cells stored at 85 °C: with GME (solid line), ME (long dashed line), GOE (short dashed line) and OE (dotted line).

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