The Application of Room Temperature Molten Salt with Low Viscosity to the Electrolyte for Dye-Sensitized Solar Cell

Hajime Matsumoto,* Toshihiko Matsuda,† Tetsuya Tsuda,†† Rika Hagiwara,†† Yasuhiko Ito,†† and Yoshinori Miyazaki
Department for Energy Conversion, Osaka National Research Institute, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577
†*Japan Science and Technology Corporation*
††*Graduate School of Energy Science, Kyoto University, Sakyo-ku, Kyoto 606-8501*

(Received October 20, 2000; CL-000956)

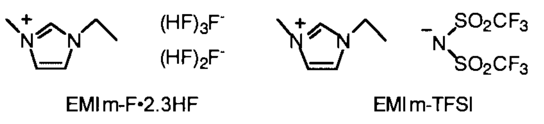
The effect of the viscosity of room temperature molten salt (RTMS) electrolyte has been investigated on the performance of dye-sensitized solar cell (DSSC). Both the short circuit photocurrent and conversion efficiency are increased with decreasing the viscosity of RTMS as in the case of conventional electrolytes. The conversion efficiency of 2.1% observed for the cell of EMIm-F•2.3HF is the highest value reported for all the DSSC consisted of RTMS.

Room temperature molten salts (RTMS) have been extensively studied for application as unique electrolytes for wet electrochemical devices like batteries because of their high ionic conductivity, electrochemical stability, and non-volatility. In particular, non-volatility is the most decisive property to ensure the long-term stability for electrochemical devices.[1–3]

Papageorgiou et al. reported that these unique properties were effective for long-term operation of the electrochemical devices such as dye-sensitized solar cells (DSSC).[4] They employed 1-hexyl-3-methylimidazolium iodide (HMImI) as an involatile electrolyte melting at lower than room temperature. However, the short circuit photocurrent (J_{sc}) of the system was smaller by one order of magnitude that usually reported in the DSSC systems using organic electrolytes such as acetonitrile. Since the slow diffusion of iodide redox species in highly viscous HMImI melt (ca. 1800 mPa s at 25 °C) causes the low J_{sc}, a low viscous RTMS have been expected to improve the conversion efficiency of the DSSC.

Recently, Hagiwara et al. succeeded to synthesize extremely low viscous RTMS based on 1-ethyl-3-methylimidazolium (EMIm) and two hydrofluoride anions, $H_2F_3^-$ and, $H_3F_4^-$ (molar ratio, 7:3), being called EMIm-F•2.3HF. The viscosity of EMIm-F•2.3HF was 4.9 mPa s at 25 °C which is the smallest among the air-stable RTMS reported so far.[5]

In the present study, the application of the EMIm-F•2.3HF to the DSSC system has been made to investigate the effect of viscosity of molten salt on the cell performance. A comparison was made using 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIm-TFSI) which shows a higher viscosity (34 mPa s at 25 °C)[2] than that of EMIm-F•2.3HF.



Scheme 1. Structures of room temperature molten salt used in this study.

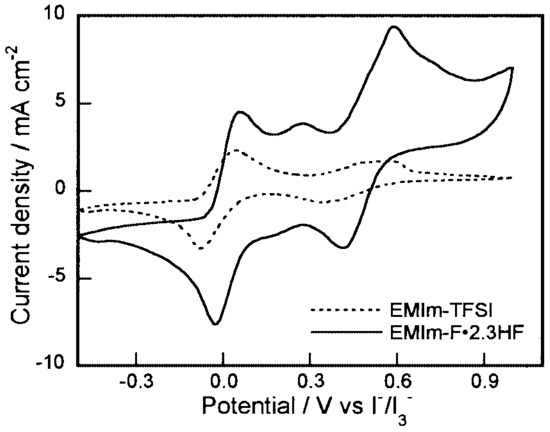


Figure 1. Cyclic voltammograms of room temperature molten salt contained 60 mM $N(n\text{-}C_3H_7)_4I$, 15 mM I_2. Scan rate: 100 mV sec^{-1}. Temperature: 25 °C. Working electrode: Pt disk (0.02 cm^2). Counter electrode: Pt (1.0 cm^2). Reference electrode: Pt wire immersed in EMIm-TFSI contained 60 mM $N(n\text{-}C_3H_7)_4I$, 15 mM I_2.

According to the literature,[6] the dye-sensitized TiO_2 (P25, Nippon Aerosil) films were prepared on glass plates coated by the F-doped SnO_2 (Asahi Glass) without $TiCl_4$ post-treatment. Counter electrodes were prepared by the deposition of platinum on glass plates using a sputtering method. The dye-coated TiO_2 and the Pt electrodes were fixed together without using sealing materials. N3 dye (Solaronix, *cis*-Ru(4,4'-dicalboxy-2,2'-bipyridine)$_2$(thiocyanato)$_2$) was used for the DSSC cell. A small quantity of the molten salt electrolytes (ca. 10 μL) including 0.9 M (mol dm^{-3}) of 1,2-dimethyl-3-hexylimidazolium iodide (DMHImI) and 30 mM of I_2 was made to permeate into the cell from the side aperture. The projection area of the cell was 1.0 cm^2. Either DMHImI or tetrapropylammonium iodide (TPAI) was combined with the iodine to provide iodide and triiodide redox couple of ions. EMIm-F•2.3HF[5] and EMIm-TFSI[2] were prepared by the literature methods. To investigate electrochemical behavior of iodide in EMIm-F•2.3HF, three-electrode electrochemical cell was used with a Pt disk elecrtrode of 1.6-mm diameter and a Pt flag (1 cm^2) electrode as a working electrode, and a counter electrode, respectively. The reference electrode was prepared in the same manner as previously described.[2] A Pt wire was immersed in EMIm-TFSI melt containing 15 mM I_2, 60 mM TPAI in a Pyrex tube separated with an porous Vycol glass.

Figure 1 shows a cyclic voltammogram for 60 mM TPAI and 15 mM I_2 in EMIm-F•2.3HF at a disk electrode. Two major redox peaks typically observed for iodide redox couple in organic solvents such as acetonitrile were found for both the EMIm-F•2.3HF and the EMIm-TFSI systems. The diffusion coefficient of triiodide ($D(I_3^-)$, (cm^2s^{-1})) in both EMIm-

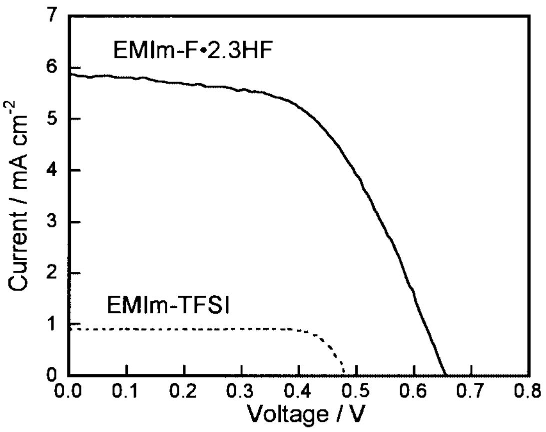


Figure 2. Photocurrent–voltage characteristics of a cell using room temperature molten salt as an involatile solvent contained 0.9 M of DMHImI and 30 mM of I_2. Temperature; 25 °C. AM 1.5 (100 mW cm^{-2}).

F•2.3HF and EMI-TFSI could be calculated from the current of the reduction peak (I_p, (A cm^{-2})) appeared at around 0.0 V vs I^- / I_3^- using the equation 1.[8]

$$I_p = (2.69\times 10^5)\, n^{3/2} A\, D(I_3^-)\, v^{1/2} C \quad \text{at } 25\ ^\circ\text{C} \qquad (1)$$

where n: electrons per molecule oxidized or reduced (=2), A: area of working electrode (cm^2), v: scan rate (V s^{-1}), C: concentration (mol cm^{-3}).

The calculated diffusion coefficients of triiodide, $D(I_3^-)$ in various solutions are increased with decreasing the viscosity of the corresponding solvent as shown in Table 1.

Figure 2 shows the I–V characteristic under the illumination of AM 1.5 (100 mW cm^{-2}). The concentration of iodide redox, 0.9 M of DMHImI and 30 mM of I_2, was determined to obtain the highest J_{sc} in the case of EMIm-F•2.3HF. The J_{sc} observed for the EMIm-F•2.3HF system was about six times larger than that of EMIm-TFSI. Such increase of the J_{sc} with the use of EMIm-F•2.3HF must be caused by the enhancement of the diffusion of triiodide as shown in Table 1. However, the conversion efficiency for EMIm-F•2.3HF was lower than that for the acetonitrile systems. This might be due to the lower diffusion coefficient of triiodide even in EMIm-F•2.3HF system. Therefore, it is necessary for improving cell performance to develop a less viscous RTMS to increase diffusion coefficient of iodide redox. However, the preparation of less viscous RTMS is difficult because a principle of molecular design to change the physical properties of RTMS such as viscosity and melting point has not been well established yet.

As shown in Table 1, it should be noted that the J_{sc} of highly viscous HMImI system is comparable to that of EMIm-TFSI system. Papageorgiou et al. previously claimed that the triiodide in HMImI, which formed after the regeneration of oxidative form of N3 dye with iodide, might be transferred to the Pt counter electrode by not a diffusion of triiodide but Grotthus-like hopping mechanism.[4] The fact that the diffusion coefficient of triiodide in HMImI shown in Table 1 is about eight times lower than that of EMIm-TFSI strongly supports the existence of such non-diffusional hopping mechanism of triiodide. It has not been clarified the accurate mechanism of hopping of triiodide in RTMS yet, however, such non-diffusional mechanism might be valid for improving cell performance using relatively high viscous RTMS as an involatile solvent.

Table 1. Cell performance in various electrolyte systems at 25 °C (AM 1.5, 100 mW cm^{-2})

Solvent	Visc[a] /mPa s	[RI][b] /M[c]	$[I_2]$ /mM	J_{sc} /mAcm^{-2}	V_{oc} /V	FF[d]	η[e] /%	$D(I_3^-)$[f] /10^{-7}cm^{2}s^{-1}
HMImI[g]	1800	4.6	50	0.8	—	—	—	0.9[g]
EMIm-TFSI	34	0.9	30	0.9	0.50	0.80	0.36	7.6
EMIm-F·2.3HF	4.8	0.9	30	5.8	0.65	0.56	2.1	43
Acetonitlile[h]	0.4	0.9	50	13.7	0.70	0.59	5.7	110[i]

[a]Viscosity of solvent. [b][RI]=[DMHImI]. [c]mol dm^{-3}. [d]Fill factor. [e]Conversion efficiency. [f]Diffusion coefficient of triiodide ion calculated from the reduction peak current of cyclic voltammogram as shown in Figure 1. [g]From ref 4. [h]The electrolyte contained 0.1 mol dm^{-3} of LiI, 0.8 mol dm^{-3} of DMHImI and 0.2 mol dm^{-3} of t-butylpyridine. [i] Calculated from the cyclic voltammogram of an acetonitlile solution containing 12 mM of TPAI and 3 mM of iodine.

We have currently studied new RTMS based on molten polyiodide, which contains iodine with high concentration (> 1000 mM) comparing with a conventional DSSC systems. The viscosity (> 40 mPa s at 60 °C) is much higher than EMI-TFSI. However, the J_{sc} of 8 mA cm^{-2} comparable to EMIm-F•2.3HF system as mentioned above was obtained. This suggests that the hopping mechanism of iodide redox couple as stated above is valid for the improving cell performance using RTMS. The detailed study will be published elsewhere.

In conclusion, the performance of DSSC system using RTMS is improved with decreasing the viscosity of RTMS. The 2.1% of conversion efficiency has been achieved with the use of the lowest viscous EMIm-F•2.3HF at present. The hopping mechanism for iodide redox will be important to improve cell performance using relatively high viscous RTMS.

References

1 J. S. Wilkes and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, **1992**, 965.

2 P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, and M. Grätzel, *Inorg. Chem.*, **35**, 1168 (1996).

3 J. Fuller, R. T. Carlin, and R. A. Osteryoung, *J. Electrochem. Soc.*, **144**, 3881 (1997).

4 N. Papageorgiou, Y. Athanassov, M. Armand, P. Bonhôte, H. Pettersson, A. Azam, and M. Grätzel, *J. Electrochem. Soc.*, **143**, 3099 (1996).

5 R. Hagiwara, T. Hirashige, T. Tsuda, and Y. Ito, *J. Fluorine Chem.*, **99**, 1 (1999).

6 M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphrybaker, E. Muller, P. Liska, N. Vlachopoulos, and M. Grätzel, *J. Am. Chem. Soc.*, **115**, 6382 (1993).

7 H. Stegemann, A. Rohde, A. Reiche, A. Schnittke, and H. Fullbier, *Electrochim. Acta*, **37**, 379 (1992).

8 A. J. Bard and L. R. Faukner, "Electrochemical Methods Fundamentals and Applications", John Wiley & Sons, New York, NY, 1980, p. 218.