

Dye-sensitized Solar Cells Using Ionic Liquid-based Electrolytes

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The influence of the concentration of I^-/I_3^- redox couples in an ionic liquid-based electrolyte was investigated for application to dye-sensitized solar cells (DSCs). 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIm-TFSI) was used as an ionic liquid. Photocurrents increased with increasing concentration of I^-/I_3^- to the maximum current and they decreased after that due to decrease of transparency of the electrolyte solution. Photo-electrode preparation conditions were also studied. The particle size of TiO_2 and thickness of a nanoporous layer had a significant effect on the photocurrent. Under the optimized conditions, energy conversion efficiency of 4.7 % was obtained in a 5 mm x 9 mm-sized cell. A cell using an ion-gel electrolyte, gelled EMIm-TFSI type electrolyte by a fluoride polymer, showed photocurrent-voltage characteristics almost equal to that using the liquid form electrolyte. These ionic liquid-based electrolytes were applied to large-sized (*i.e.*, 100 mm x 100 mm) DSCs, which had high-conductive transparent glass substrates to decrease internal resistance. Energy conversion efficiency was 2.7 % in the ionic liquid system and 2.4 % in the ion-gel system.

Key words: dye-sensitized solar cell, ionic liquid, ion-gel

1. INTRODUCTION

Dye-sensitized solar cells (DSCs) comprised of nanocrystalline TiO_2 , sensitizing dyes and electrolyte solutions [1] are attracting much interest because of low fabrication costs, simple manufacturing processes, no toxic materials using, and so on. In DSCs, incident light is absorbed by sensitizing dyes, and electrons from the photoexcited dyes are injected into the conduction band of a semiconductor (TiO_2). Dyes are subsequently reduced by an electrolyte with redox couples, typically I^-/I_3^- . Generally, a volatile solvent (*e.g.*, acetonitrile) has been employed for an electrolyte solution. When a volatile solvent is used, devices lose long-term stability due to its evaporation. Replacing of the volatile-type electrolyte to a non-volatile material has been attempted to avoid this problem.

Ionic liquids seem to be suitable for the electrolyte material of DSCs because of their favorable properties such as non-volatility, non-flammability and thermal and electrochemical stability. Various ionic liquids have been studied for DSCs [2-5] and improvement of thermal and longitudinal stability was reported. On the other hand, some issues are involved in the application of ionic liquids as electrolyte materials. In ionic liquids, physical diffusion of redox species was slow due to their high viscosity [3]. This led to lower photocurrent as compared with a conventional volatile electrolyte system. It is necessary to optimize electrolyte compositions and photo-electrode preparation conditions for the ionic liquid-based electrolyte system. Solidification of the electrolyte is also requisite to prevent leakage of the electrolyte when cells are broken or in the manufac-

turing process. An ion-gel electrolyte, which was a physically or chemically gelled ionic liquid-type electrolyte, has been studied. As a gelator, for example, a low molecular weight agent [4], a fluoride polymer [6] and a chemically crosslinked agent [7,8] have been applied. For the practical use of DSCs, it is necessary to enlarge the cell from small laboratory-size to practical-size that has at least several square centimeters or more of the photo-electrode. Two strategies, namely, the interconnecting of many small cells and the enlargement of the photo-electrode area with a current collector, were previously reported [9].

In this report, we investigated electrolyte compositions (*e.g.*, as a function of I^-/I_3^- redox content), polymer-gelated electrolyte properties using the ionic liquid. In addition, large-sized DSCs using those materials were fabricated.

2. EXPERIMENTAL

1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIm-TFSI), as shown in Fig. 1, was used as an ionic liquid. EMIm-TFSI was prepared by anion exchange reaction from 1-ethyl-3-methylimidazolium bromide and lithium bis(trifluoromethanesulfonyl)imide. The electrolyte solution was composed of 0.15 M I_2 , 1.5 M 1-ethyl-3-methylimidazolium iodide (EMIm-I), 0.1 M LiI and 0.5 M 4-*tert*-butylpyridine (TBP) dissolved in EMIm-TFSI. It was assumed that I^- and I_2 immediately formed I_3^- in the electrolyte solution when they were mixed. A small amount of water, less than 1 wt%, was added to the electrolyte solution before measurement. For preparation of an ion-gel electrolyte, the ionic

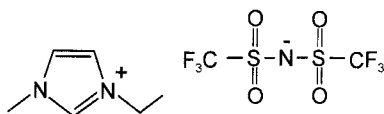


Fig. 1 Structure of an ionic liquid; EMIm-TFSI.

liquid-type electrolyte solution was gelled by poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) (VdF : HFP = 85 : 15). A volatile electrolyte solution, as a reference, was composed of 0.05 M I_2 , 0.3 M 1,2-dimethyl-3-propylimidazolium iodide, 0.1 M LiI and 0.5 M TBP in methoxyacetonitrile.

A typical photo-electrode in this study, which had 9 mm x 5 mm area, was prepared as follows. TiO_2 dispersed paste (Nanoxide T, Solaronix SA) was deposited on a conducting glass substrate (FTO; fluoride-doped SnO_2 overlayer) (8-10 Ω /square) using a doctor-blade technique. After drying a wet film on the substrate, the film was sintered at 450 $^{\circ}C$. A light-reflecting layer using several hundred micrometers-sized TiO_2 particles was formed on the prepared nano-porous TiO_2 layer by the same procedure. Sintering time was totally 60 min. Coating of the TiO_2 surface with dyes was carried out by soaking the substrate with the nanoporous TiO_2 layer overnight in a solution of ruthenium (2,2'-bipyridyl-4,4'-dicarboxylic acid) $_2$ (NCS) $_2$ (N3 dye) at room temperature. As a counter-electrode, an FTO substrate on which Pt had been deposited by sputtering was used. The photo-electrode and the counter-electrode were stacked and then an intervening space between each electrode was filled with the electrolyte to fabricate DSCs. In the case of using the ion-gel electrolyte, a tetrahydrofuran solution containing PVdF-HFP and a liquid form electrolyte was repeatedly cast on the electrode to deposit an electrolyte layer.

Photoelectrochemical measurements of cells were performed using SI1286 electrochemical interface (Solartron, formerly Schlumberger) and MP-160 DC electronic load (Eiko Seiki) under simulated solar light (AM 1.5, 100 mW/cm^2 , ESS-150A, Eiko Seiki).

3. RESULTS AND DISCUSSION

3.1 Photovoltaic properties of EMIm-TFSI type cells

Dependence of short-circuit current (I_{sc}) of the cell on the concentration of I/I_3^- is shown in Fig. 2. When the concentration of I/I_3^- redox couples was equivalent to that in the volatile electrolyte system as a reference, I_{sc} values were very low. I_{sc} increased with increasing concentration to the maximum current. After that, it decreased. The increase of the photocurrent was attributed to increase of charge transport media, and the decrease of the current seems to be the result of decrease of transparency of the electrolyte solution. It was reported that the charge transfer rate in an ionic liquid system is significantly enhanced by a contribution of the exchange reaction when the I/I_3^- ratio was comparable and I/I_3^- concentration was high [5]. However, it was considered that the above-mentioned electrolyte composition could not be utilized effectively for the present cells as shown in Fig. 2 because of increase of light absorption by I_3^- in the electrolyte solution. Open-circuit voltage (V_{oc}) of cells was decreased with increasing the concentration of I/I_3^- . In this system,

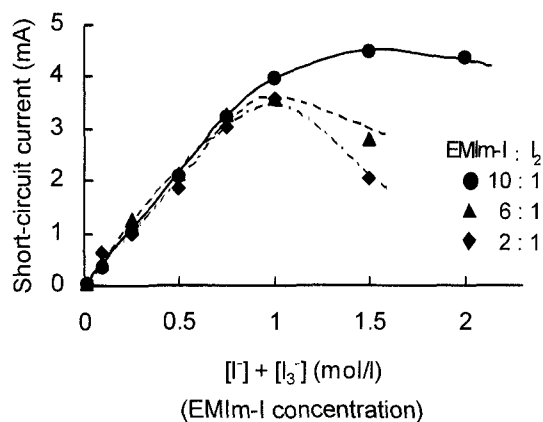


Fig. 2 Dependence of short-circuit current on the concentration of I/I_3^- redox couples in the EMIm-TFSI type electrolyte.

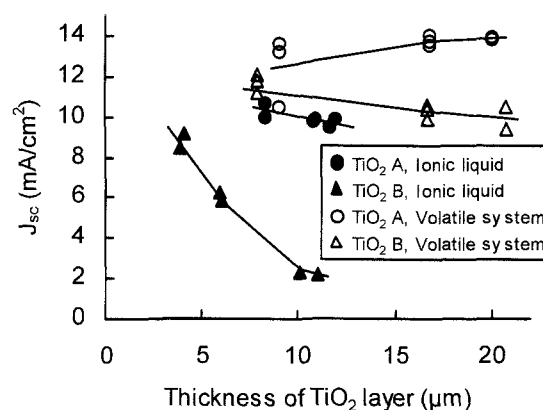


Fig. 3 Dependence of short-circuit current density (J_{sc}) on thickness of the nano-porous TiO_2 layer in the ionic liquid electrolyte system or volatile electrolyte system. Particle size was Φ 13-20 nm (TiO_2 A) and Φ 6-9 nm (TiO_2 B).

experimental cell performance was favorable in the composition that EMIm-I (1.5 M) : I_2 = 10 : 1. It was considered that physical diffusion of the redox species mainly dominated the charge transport in this electrolyte composition.

The influence of TiO_2 particle size on the cell performance was investigated. The diffusion of I/I_3^- within nano-pores of the TiO_2 layer was slower than that in the bulk of the electrolyte [10]. In the case of a viscous ionic liquid system, the influence of nano-pore size might be more remarkable. Figure 3 shows dependence of short-circuit current density (J_{sc}) on thickness of the nano-porous TiO_2 layer in different-sized TiO_2 particles (TiO_2 A: Φ 13-20 nm, TiO_2 B: Φ 6-9 nm). The smaller-sized particles (TiO_2 B) system showed comparatively large J_{sc} values in a thinner thickness range because TiO_2 B had a very large BET surface area (220 g/m^2 , cf. TiO_2 A: 80 g/m^2). However, J_{sc} significantly decreased with increasing thickness unlike the larger particles (TiO_2 A) system. On the other hand, in the case of using a volatile electrolyte, the remarkable decreasing tendency was not observed up to

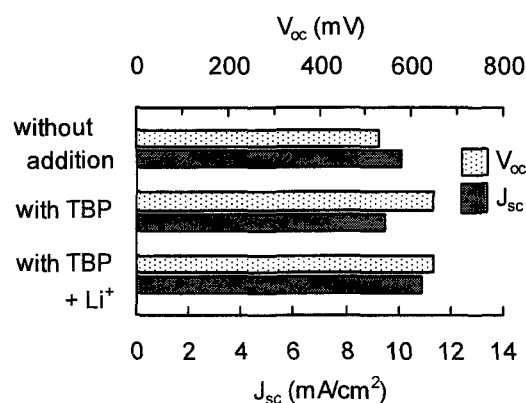


Fig. 4 Effect of addition of TBP (0.5 mol/l) and LiI (0.1 mol/l) on cell performance in the EMIm-TFSI electrolyte system.

a thicker range in either particles used.

When the EMIm-TFSI type electrolyte included only iodine redox couples, the cell performance was poor with low V_{oc} as compared with the volatile electrolyte system. The low V_{oc} was attributed to the difference in redox potential of the electrolyte and increasing of recombination of electrons with I_3^- due to dense iodine redox couples. Figure 4 shows the effects of additive agents to V_{oc} and J_{sc} in EMIm-TFSI type cells. The addition of TBP [11] and Li^+ could decrease recombination and improve voltage and current performance. After optimization of the condition, energy conversion efficiency (η) of 4.7 %, which was about 70% of the output of the volatile electrolyte system, was attained in the EMIm-TFSI system as shown in Fig. 5.

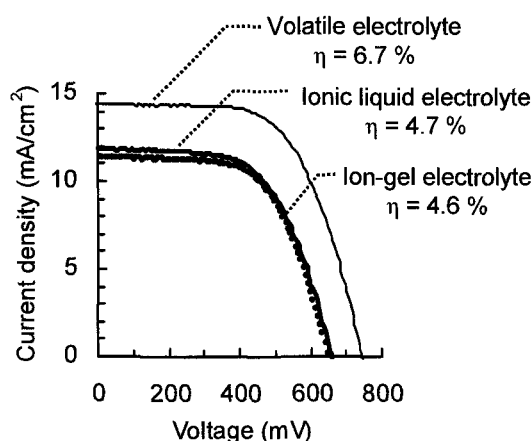


Fig. 5 I-V characteristics of cells using the ionic liquid electrolyte (—), the ion-gel electrolyte (••••), the volatile electrolyte (—). Photo-electrode size was 5 mm x 9 mm.

3.2 Quasi-solidification of the electrolyte

Performance of ion-gel type cells was also investigated. Gelation of the EMIm-TFSI type electrolyte solution was carried out using PVdF-HFP as a gelator. It was possible to gelate the electrolyte solution even with small quantitative PVdF-HFP addition of several percent or less. As shown in Fig. 5, the prepared ion-gel type cell had an I-V characteristic that was almost equal to

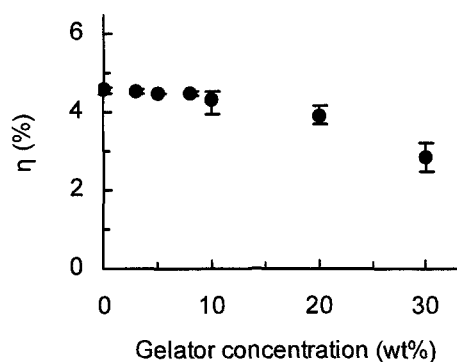


Fig. 6 Dependence of energy conversion efficiency (η) of ion-gel cells on the PVdF-HFP gelator concentration in the electrolyte.

that of the ionic liquid system. It means that serious inhibition of the charge transport due to the gelation did not occur. Figure 6 shows dependence of η on PVdF-HFP gelator concentration in the electrolyte. When the gelator content was less than 10 wt%, remarkable decrease of η values to the result of liquid form electrolyte was not observed regardless of gelator content. Therefore, it was found that this ion-gel electrolyte system could be quasi-solidified without output decrease in a range of gelator concentration mentioned above. In more than 10 wt% gelator content, η values showed a decreasing tendency and wide fluctuation.

3.3 Large-size cells using ionic liquid-based electrolytes

The EMIm-TFSI type electrolytes were applied to 100 mm x 100 mm-sized DSCs. Conductivity of a glass substrate for the photo-electrode, which was covered with transparent conductive oxide (TCO), is not high enough to apply to a large-sized cell. Thus, internal resistance of cells is increased, causing large ohmic losses. For the purpose of reducing resistance, we developed a high-conductive transparent glass electrode that had an FTO/ITO double layer (2-3 Ω /square) [12] and current-collecting metal grids (*e.g.*, made of nickel, to be published). A TCO glass substrate for DSCs required properties that were not only highly conductive but also chemically and electrochemically passive against the electrolyte solution including I^-/I_3^- redox couples. Figure 7 shows an external view of the fabricated large-sized cell with the ionic liquid-based electrolyte. The cell had a photo-electrode area of 81 cm² and an active area of 69 cm² (opening area: 85 %). The results of photoelectrochemical measurements on the large-sized cell are listed in Table I. η was 2.7 % in the ionic liquid system and 2.4 % in the ion-gel system, respectively, on the active area. Performance of a simple large-sized cell without resistance reduction (as a reference sample) was very poor. On the other hand, prepared cells with the high-conductive substrate showed dramatically improved energy conversion characteristics. Particularly, FF and J_{sc} were widely increased. At this time, for the large-sized cell, difference in output between the ionic liquid-based electrolyte system and the volatile electrolyte system was larger than the result obtained by the small-cell study. This might be due to incompleteness of some

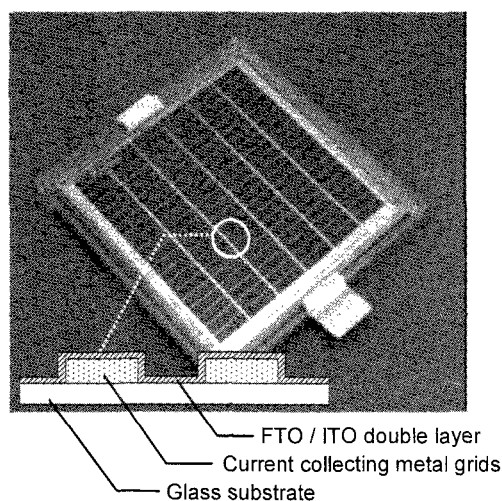


Fig. 7 A view of 100 mm x 100 mm ionic liquid-type DSC. The inset is cross-sectional structure of the transparent conductive glass electrode with current-collecting grids.

Table I Photoelectrochemical properties of large-sized cells in various electrolyte systems.

Electrolyte	I_{sc} (mA)	V_{oc} (mV)	FF	η (%) (Total Area)	η (%) (Active Area)
Ionic liquid electrolyte	484	651	0.56	2.3	2.7
Ion-gel electrolyte	401	622	0.61	2.0	2.4
Volatile electrolyte	802	742	0.56	4.3	5.1
Ionic liquid electrolyte without grids *	99	582	0.26		0.2

* As a reference, on a commercial FTO substrate (8-10 Ω/\square)

conditions for the cell preparation (e.g., distance between photo- and counter-electrode) that could not be fitted in with the optimized small-cell. But then, these results imply that our large-sized cells with the FTO/ITO double layer and the current-collecting grids have accomplished decrease of ohmic losses and show potential as practical DSCs technology.

4. CONCLUSION

Photovoltaic properties of DSCs using EMIm-TFSA type electrolyte were described. Cells, which showed favorable photovoltaic properties, had higher concentration of redox species as compared with that in the conventional volatile electrolyte system. The photocurrent increased with increasing concentration of iodine redox couples and it decreased after reaching the maximum value due to decrease of transparency of the electrolyte solution. At the optimized condition, energy conversion efficiency of 4.7 % was obtained in a 5 mm x 9 mm-sized cell. In addition, quasi-solidification of an ionic liquid type electrolyte was successful without notable decrease cell performance by use of PVdF-HFP.

These ionic liquid-based electrolytes were applied to large-sized DSCs using low-resistance photo-electrode. Energy conversion efficiency was 2.7 % in the ionic liquid system and 2.4 % in the ion-gel system, respectively (on active area). At this time, cell performance of the ionic liquid system has yet been not achieved beyond the output of the volatile electrolyte system. It is considered that further development, such as utilization of a dense iodine redox system and a thin electrolyte layer, is necessary.

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