Specific Charge Transport of an Iodide / Tri-iodide Redox Couple in Ionic Liquids

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INTRODUCTION

Dye-sensitized solar cells present an important alternative to current solar technology. Photo-electrochemical cells based on sensitization of nano-crystalline TiO_2 by molecular dyes have attracted great attention since their recognition as efficient photovoltaic devices. Usually, an iodide/tri-iodide redox (I^-/I_3^-) active couple dissolved in organic solvents is used for the electrolyte, which has restricted use for the evaporation of solvent. Ionic liquids, due to their unique properties such as non-volatility, non-flammability, relatively high conductivity and gel-forming property with polymers, have also been applied to the solar cells. However, fundamental properties of an (I^-/I_3^-) redox couple in ionic liquids, including the equilibrium potentials and the charge transport mechanism, have not been revealed yet. In this study, we elucidate the fundamental properties of an ionic liquid and ion gels using ultra-microelectrode technique and discuss the prospect of the redox active ionic liquids as the charge transport layer of the solar cells.

EXPERIMENTAL

1-Ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide (EMImTFSI) was used as the ionic liquid, and EMImI and I_2 were dissolved in it as a redox couple. An ultra-microelectrode technique was employed for the electrochemical measurements in order to simplify determination of the transport property of the redox couple from steady-state voltammetry. A platinum microdisk electrode (12 μm diameter) was used as the working electrode, while a platinum (0.3 mm diameter) disk electrode was used as the counter electrode. Steady-state microelectrode voltammograms of EMImI/I_2 mixtures were obtained. Since the redox responses are dependent on the [EMImI]/[I_2] ratios, the reactions occurring in the ionic liquid can be assigned.

RESULTS AND DISCUSSIONS

Limiting currents (I_{lim}) in these measurements, corresponding to the reaction (I_3^- +2e^- ⇄ 3I^-), which is believed to occur in the solar cells, are given by

$$I_{lim} = 4nFDcr.$$

D is the average diffusion coefficient of I^- and I_3^- and seems to include both physical diffusion and exchange-reaction-based-diffusion in such viscous media. When diffusion coefficient includes physical diffusion and exchange-reaction-based-diffusion, D is expressed by

$$D = D_{phys} + 1/6k_{ex}\delta^2 c$$

where k_{ex} is the self-exchange rate constant, δ is the center-to-center interstice distance at transfer reaction. The limiting currents were measured by changing both EMImI concentration and the [EMImI]/[I_2] ratios. Non-linearity of the limiting currents allows us to separate the physical diffusion and the exchange-reaction-based-diffusion between I^- and I_3^-. The contribution of the exchange reaction becomes predominant when the

concentration is high, and [I^-] and [I_3^-] are comparable (Table 1)[1].

Table 1 Physical diffusion (D_{phys}) and exchange-reaction-based diffusion (D_{ex}) coefficients of EMImI / I_2 in EMImTFSI.

$I^- : I_2$	D_{phys} / 10^{-7} cm^2 s^{-1}	D_{ex} / 10^{-7} cm^2 s^{-1}		R^2
		0.01 M	1.0 M	
1 : 1	2.74	-	-	0.997
1.5 : 1	2.83	0.094	9.40	0.981
2 : 1	2.63	0.035	3.5	0.988
3 : 1	0.49	0.053	5.3	0.995
4 : 1	0.93	0.025	2.5	0.996
6 : 1	1.28	0.008	0.76	0.997
8 : 1	1.72	0.005	0.48	0.999
10 : 1	1.98	-	-	0.992
10 : 0	2.68	-	-	0.997
$EMIm^+$	6.35[3]	-	-	-
$TFSI^-$	3.54[3]	-	-	-

Performances of solar cells with the ionic liquids as their electrolytes have been investigated in detail. In spite of their high viscosities, the solar cells with the ionic liquid electrolytes exhibit relatively high performances. Especially, the photocurrent density reaches higher than 80% of the cell with organic solvents[2], although the viscosity of the ionic liquid electrolytes is more than 10 times higher than that of the organic solvents. The main reason for this phenomenon seems to be caused by the contribution of the exchange-reaction-based diffusion process between I^- and I_3^- dissolved in the ionic liquids as a redox couple. Similar results could also be obtained for ion gels as the electrolytes.

REFERENCES

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