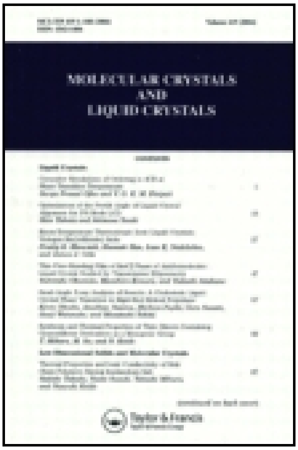

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Influence of Ionic Liquids in Quasi-Solid State Electrolyte on Dye-Sensitized Solar Cell Performance

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Room temperature ionic liquids have been used as electrolytes to investigate the performance and the characteristics in dye-sensitized solar cells (DSSCs). We focused on quasi-solid state electrolyte using ionic liquids, which are non-volatile liquids having relatively high conductivities. We studied the performance of the DSSC device with different anion or cation structures of ionic liquids. The power conversion efficiency of the DSSC device using $[EMIm]^+[PF_6]^-$ under $100\,mA/cm^2$ is achieved up to 4.37%.

Keywords: dye-sensitized solar cells; ionic liquids; photovoltaic performance; quasi-solid state electrolyte

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INTRODUCTION

Dye-sensitized solar cells (DSSCs) are attractive for next generation solar cells not only because of their potentially high conversion efficiency but also the lower production cost of DSSCs than that of conventional amorphous silicon solar cells [1]. However, improvement in the long term stability of DSSCs, due to the evaporation of the liquid electrolyte, is an important requirement for practical use. In order to solve this problem partially, we focused on quasi-solid sate electrolyte using ionic liquids. Ionic liquids are room temperature molten salts that consist of cations and anions. An ionic liquid has unique properties such as non-volatility, nonflammability, and electrochemical stability, so that utilization in a wide range of electrochemical devices has been expected. The use of ionic liquids for DSSCs [2–6] is one of the fascinating applications of ionic liquids, because DSSCs present an important alternative to current solar technology. Various ionic liquids have been studied as electrolyte materials for DSSC since it has been reported by Gratzel group [2], and especially, those with 1,3-dialkylimidazolium cations were used well. The influence of various ionic liquids in quasi-solid state electrolyte on photovoltaic performance of DSSC was investigated. The properties of ionic liquids can be tuned by controlling the structures of anions and cations [7]. However, the structural effect of ionic liquids on the performances of DSSCs has not been revealed.

In this paper, we studied the effect of the anion or cation structures of ionic liquids on performance of DSSC device.

EXPERIMENTAL

The working electrode was prepared as follows. The TiO_2 paste with 9 nm particle size (Ti-Nanoxide HT/SP, Solaronix Co) was placed on an FTO glass by doctor blade method, followed by sintering at 120°C for about 40 min and at 450°C for about 60 min in air to give a TiO_2 electrode with an effective area of 0.25 cm^2, and a TiO_2 film thickness of 10 μm. The nanoporous TiO_2 electrode was dipped in dye solution that dye was dissolved in a concentration of 10 mg of cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) dye (N3 dye, Solaronix Co) per 50 ml of absolute ethanol solution at room temperature over night. The dye adsorbed TiO_2 electrode was dipped in electrolyte solution at room temperature for 24 hours. Polymer electrolyte are contained of I_2, TBAI, ionic liquids, EC/PC (EC: PC = 4:1 v/v), PAN (M_w = 20,000, Aldrich Co) as

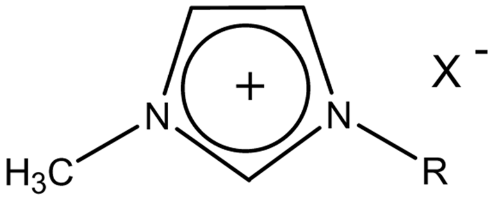

FIGURE 1 The chemical structure of an ionic liquid.

polymer matrix. 1-Ethyl-3-methylimidazolium iodide ($[EMIm]^+[I]^-$), 1-ethyl-3-methylimidazolium chloride ($[EMIm]^+[Cl]^-$), 1-ethyl-3-methylimidazolium tetrafluoroborate ($[EMIm]^+[BF_4]^-$), 1-ethyl-3-methylimidazolium hexafluorophospate ($[EMIm]^+[PF_6]^-$), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ($[EMIm]^+[CF_3SO_3]^-$), 1-ethyl-3-methylimidazolium nitrate ($[EMIm]^+[NO_3]^-$), 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMIm]^+[BF_4]^-$), 1-hexyl-3-methylimidazolium tetrafluoroborate ($[HMIm]^+[BF_4]^-$), and 1-octyl-3-methylimidazolium tetrafluoroborate ($[OMIm]^+[BF_4]^-$) were used as ionic liquids. Chemical structures of various ionic liquids are shown in Figure 1 and Table 1. After that, the electrolyte was casted onto dye adsorbed TiO_2 electrode and was dried at about 60℃ for 2 hours.

The counter electrode was also prepared by the similar method that TiO_2 film was coated. Pt paste (Pt catalyst T/SP, Solaronix Co) was placed on an FTO glass by doctor blade method, followed by sintering to at 100℃ for about 10 min prior firing at 450℃ for about 50 min in air. In assembling of DSSC devices, the working electrode and the counting electrode were clamped together and the intervening space between two electrodes was filled the polymer electrolyte.

TABLE 1 R-, X- Groups of Various Ionic Liquids

	R-	X-
$[EMIm]^+[BF_4]^-$	Ethyl	BF_4
$[BMIm]^+[BF_4]^-$	Butyl	BF_4
$[HMIm]^+[BF_4]^-$	Hexyl	BF_4
$[OMIm]^+[BF_4]^-$	Octyl	BF_4
$[EMIm]^+[Cl]^-$	Ethyl	Cl
$[EMIm]^+[I]^-$	Ethyl	I
$[EMIm]^+[NO_3]^-$	Ethyl	NO_3
$[EMIm]^+[CF_3SO_3]^-$	Ethyl	CF_3SO_3
$[EMIm]^+[PF_6]^-$	Ethyl	PF_6

The thickness of TiO_2 layer and polymer electrolyte films were measured by using Scanning Electron Microscope (SEM) and Alpha-step IQ. The surfaces of TiO_2 film, dyes adsorbed TiO_2 film were investigated by SEM. Measurement of the I-V characteristics of devices was carried out using a Solar Simulator (300 W simulator, models 81150) under simulated solar light with ARC Lamp power supply (AM 1.5, 100 mW/cm^2).

RESULTS AND DISCUSSION

We have fabricated DSSC devices using ionic liquid-based polymer electrolyte. Figure 2 shows the structure of the DSSC device. The thicknesses of the cells were about 10 μm of nanocrystalline porous TiO_2 film and 3 μm of polymer electrolyte film. We have chosen a wide variety of ionic liquids to investigate the structural effect of ionic liquids on the DSSC performances. The photocurrent-voltage characteristics of DSSC devices using ionic liquid-based polymer electrolyte on different anions and cations were shown in Figure 3, and their characteristics were summarized in Table 2 and Table 3.

Even at the same redox concentration and the same $I^{3-}/I^-{}_3$ ratio, the DSSC device performances considerably depend on the structures of the ionic liquids. The J_{sc} for the devices using $[EMIm]^+[PF_6]^-$ and $[EMIm]^+[NO_3]^-$ are relatively high, and the J_{sc} of $[EMIm]^+[Cl]^-$ is the lowest, possibly due to the size of anion. In addition to increasing ion-ion separations, larger anions can allow greater charge delocalization. As the size of the anion increases, due to the increase of ion-ion separations, the electron transfer from polymer electrolyte to nanoporous TiO_2 film becomes easy. And it can attribute to increase the J_{sc} of the DSSC device. As a result, the DSSC device using $[EMIm]^+[PF_6]^-$

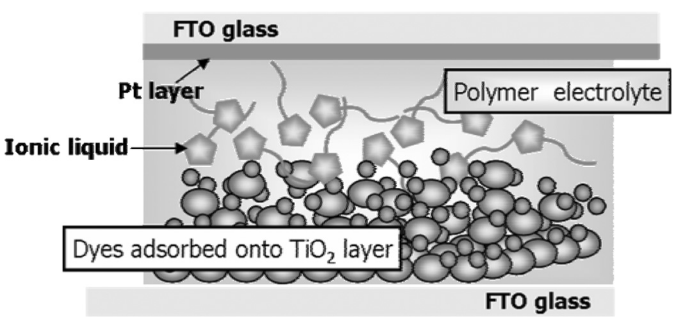

FIGURE 2 The structure of the DSSC device.

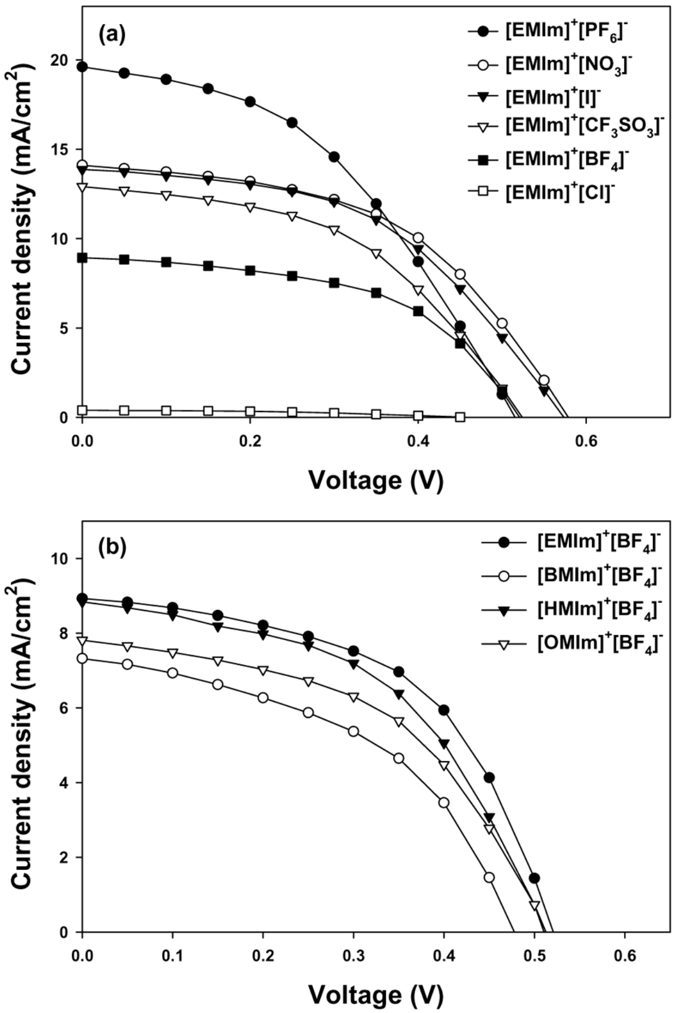

FIGURE 3 The photocurrent-voltage characteristics of the DSSC devices using ionic liquid-based polymer electrolyte (a) on different anions (b) on different cations under AM 1.5; light density: 100 mA/cm^2; active area: 0.25 cm^2.

exhibits the highest value of power conversion efficiency of 4.37% among the studied devices.

Figure 4 shows the dependences of V_{oc}, J_{sc}, FF, and efficiency on the different alkyl chain length of cations in ionic liquids. At the same anion of $[BF_4]^-$, in order to know the dependence of the performances of DSSC devices on the alkyl chain length of cations in ionic liquids,

TABLE 2 The Photovoltaic Characteristics of the DSSC Devices Using Ionic Liquid-Based Polymer Electrolyte on Different Anion Under AM 1.5 Illumination

	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	Eff. (%)
$[EMIm]^+[PF_6]^-$	0.52	19.61	0.43	4.37
$[EMIm]^+[NO_3]^-$	0.58	14.11	0.49	4.01
$[EMIm]^+[I]^-$	0.57	13.87	0.49	3.88
$[EMIm]^+[CF_3SO_3]^-$	0.52	12.91	0.48	3.22
$[EMIm]^+[BF_4]^-$	0.51	8.65	0.47	2.06
$[EMIm]^+[Cl]^-$	0.48	0.39	0.40	0.07

TABLE 3 The Photovoltaic Characteristics of the DSSC Devices Using Ionic Liquid-Based Polymer Electrolyte on Different Cations Under AM 1.5 Illumination

	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	Eff. (%)
$[EMIm]^+[BF_4]^-$	0.51	8.65	0.47	2.06
$[BMIm]^+[BF_4]^-$	0.48	7.32	0.47	1.63
$[HMIm]^+[BF_4]^-$	0.51	8.84	0.50	2.24
$[OMIm]^+[BF_4]^-$	0.51	7.81	0.49	1.98

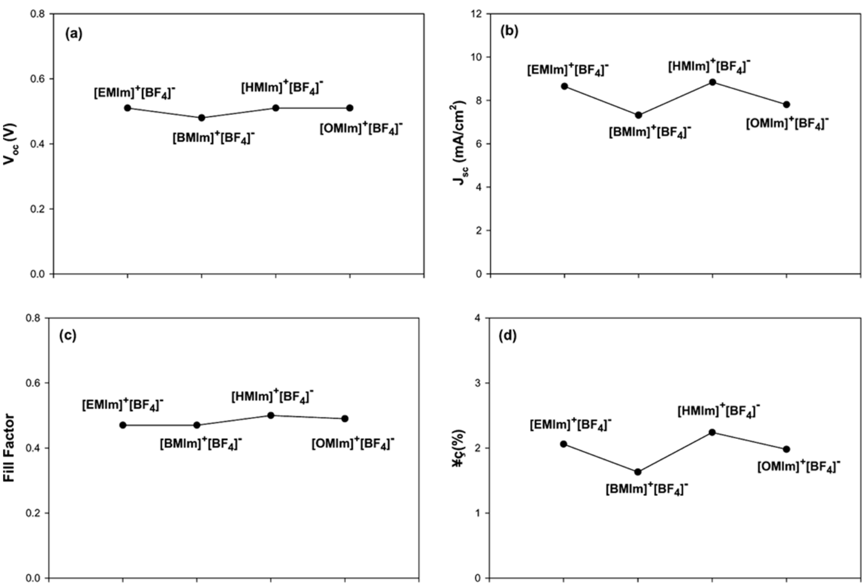

FIGURE 4 The dependence of performances of DSSC device on the different alkyl chain length of cations in ionic liquids. V_{oc} (a); J_{sc} (b); FF (c); and η (d).

DSSC devices using ionic liquids substituted by the several alkyl groups were fabricated. However, the great change could not be observed by these studies.

CONCLUSION

In this study dye-sensitized solar cell (DSSC) devices were successfully prepared using ionic liquid-based polymer electrolyte. We confirmed the effect of the anion or cation structures of ionic liquids on performance of the DSSC device. At the same cation of $[EMIm]^+$, device using $[EMIm]^+[PF_6]^-$ has the highest value of J_{sc}, while $[EMIm]^+[Cl]^-$ has the lowest value of J_{sc}. This improvement of J_{sc} resulted from the increased ion-ion separation by the increase of anion size. The increase of ion-ion separations can be the important role that it makes the electrons easily transfer from polymer electrolyte to nanoporous TiO_2 film. As a result, the power conversion efficiency of DSSC devices was improved. At the same anion of $[BF_4]^-$, DSSC devices using imidazolium salts substituted by the several alkyl groups were fabricated; however, the great change could not be observed by these studies.

The power conversion efficiency of the DSSC device using ionic liquid-based polymer electrolyte can be optimized up to 4.37%. Ionic liquids have the ideal properties as DSSC electrolytes such as non-volatility, non-flammability, and thermal and chemical stability.

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