Dye-Sensitized Solar Cells Based on Quaternary Phosphonium Ionic Liquids as Electrolytes

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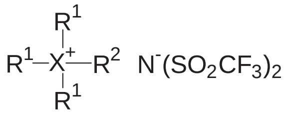
Dye-sensitized solar cells using quaternary phosphonium ionic liquids as their electrolytes have been successfully fabricated. Of these, the best device performance was achieved by using triethyl(pentyl)phosphonium bis(trifluoromethylsulfonyl)amide, whose energy conversion efficiencies were determined to be 1.2% and 3.8% under full (AM 1.5, 100 mW cm^{-2}) and low intensity (7 mW cm^{-2}) sunlight illumination, respectively. Interestingly, the energy conversion efficiencies for the quaternary phosphonium ionic liquid electrolytes are higher than those for the corresponding quaternary ammonium ionic liquids.

Dye-sensitized solar cells (DSCs) are currently receiving significant attention because of their potential applications as flexible, colorful, and low-cost solar cells.[1–5] A typical dye-sensitized solar cell consists of a dye-adsorbed nanoporous titanium dioxide (TiO_2) electrode, an electrolyte containing an iodide/triiodide redox couple and a platinum-coated conducting glass electrode. For practical applications, common organic electrolytes have a serious drawback of electrolyte evaporation causing low stability of the cells. Room temperature ionic liquids are promising candidates for replacement of the volatile organic electrolytes because of their negligible vapor pressure and high ionic conductivity.[6–10] Although a great deal of interest has been given to nitrogen-based ionic liquids such as imidazolium, quaternary ammonium, and pyridinium salts, there have been very few investigations of phosphonium-based ionic liquids.[11–13]

Recently, we have synthesized novel low-viscosity quaternary phosphonium ionic liquids as nonvolatile and highly ionic conductive electrolytes.[14] It was found that the tetraalkylphosphonium-based ionic liquids were chemically, electrochemically, and thermally stable. These characteristics make them suitable as electrolytes of DSCs. In this work, we investigate DSCs using triethyl(pentyl)phosphonium bis(trifluoromethylsulfonyl)amide (P_{2225}-TFSA) and tributyl(methyl)phosphonium bis(trifluoromethylsulfonyl)amide (P_{4441}-TFSA) as electrolytes (Fig. 1). In addition, we compare them with the corresponding quaternary ammonium-based ionic liquids, triethyl(pentyl)ammonium bis(trifluoromethylsulfonyl)amide (N_{2225}-TFSA) and tributyl(methyl)ammonium bis(trifluoromethylsulfonyl)amide (N_{4441}-TFSA).



$$R^1{-}\overset{\overset{R^1}{|}}{\underset{\underset{R^1}{|}}{X^+}}{-}R^2 \quad N^-(SO_2CF_3)_2$$

P_{2225}-TFSA : X = P, $R^1 = C_2H_5$, $R^2 = C_5H_{11}$
N_{2225}-TFSA : X = N, $R^1 = C_2H_5$, $R^2 = C_5H_{11}$
P_{4441}-TFSA : X = P, $R^1 = C_4H_9$, $R^2 = CH_3$
N_{4441}-TFSA : X = N, $R^1 = C_4H_9$, $R^2 = CH_3$

Fig. 1. Molecular structures of quaternary phosphonium and ammonium ionic liquids.

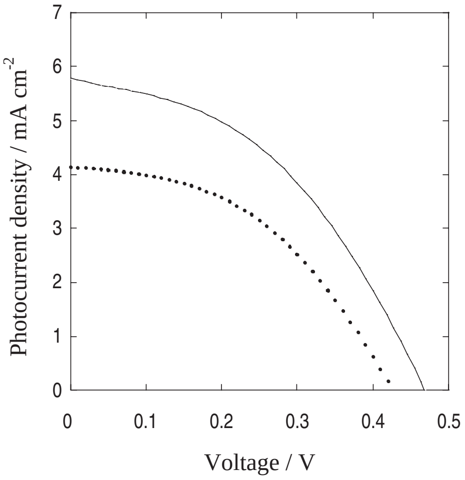


Fig. 2. Photocurrent density–voltage characteristics of the DSC devices based on P_{2225}-TFSA (solid line) and N_{2225}-TFSA (dotted line) ionic liquid electrolytes under AM 1.5 simulated full sunlight (100 mW cm^{-2}) illumination. Each electrolyte contains iodide/triiodide redox couple ($[I^-]:[I_2] = 10:1$, $[I^-] + [I_3^-] = 1.0\,\mathrm{mol\,L^{-1}}$) in each ionic liquids.

Figure 2 shows photocurrent–voltage curves of the DSCs based on P_{2225}-TFSA (P_{2225}-I/I_2) and N_{2225}-TFSA (N_{2225}-I/I_2) electrolytes ($[I^-]:[I_2] = 10:1$, $[I^-] + [I_3^-] = 1.0\,\mathrm{mol\,L^{-1}}$) under full sunlight illumination (AM 1.5, 100 mW cm^{-2}). Short-circuit current (J_{sc}) and open-circuit voltage (V_{oc}) of the DSC using P_{2225}-TFSA were higher than those using N_{2225}-TFSA, whereas the values of fill factor (*ff*) were almost same as for N_{2225}-TFSA. Photovoltaic parameters of the DSCs based on various ionic liquids are summarized in Table 1. Of those, the best device performance was achieved by using P_{2225}-TFSA as the electrolyte, whose energy conversion efficiency (η) was 1.2% under full sunlight illumination. This value is not so high compared with methoxyacetonitrile or imidazolium ionic-liquid-based DSCs;[8] however, it must be pointed out that J_{sc}, V_{oc}, and η of the phosphonium ionic-liquid-based cells were higher than those of the corresponding ammonium-based cells, whereas the fill factors were almost same.

It is well known that the performance of the DSC is affected by the viscosity and conductivity of the electrolyte. Physical

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Table 1. Photovoltaic Parameters of the DSCs Using Ionic Liquid as Electrolytes[a)]

	J_{sc} /mA cm^{-2}	V_{oc} /mV	*ff*	η/%
P_{2225}-TFSA	5.8	470	0.43	1.2
N_{2225}-TFSA	4.1	427	0.45	0.8
P_{4441}-TFSA	4.1	475	0.44	0.9
N_{4441}-TFSA	2.5	454	0.44	0.5

a) $[I^-]$:$[I_2]$ = 10:1, $[I^-] + [I_3^-] = 1.0\,\mathrm{mol\,L^{-1}}$, AM = 1.5 (100 mW cm^{-2}) illumination, cell active area = 0.283 cm^2.

Table 2. Physical Properties of the Ionic Liquids[14]

	Viscosity[a)] /mPa s	Conductivity[a)] /mS cm^{-1}	T_{dec}[b)]/°C
P_{2225}-TFSA	88	1.73	380
N_{2225}-TFSA	172	0.98	385
P_{4441}-TFSA	207	0.42	379
N_{4441}-TFSA	631	0.31	380

a) Data at 25 °C. b) Thermal decomposition temperature of 10% weight loss.

properties of the ionic liquids are summarized in Table 2.[14] The viscosities of P_{2225}-TFSA and N_{2225}-TFSA, which have shorter alkyl chains, are lower than those of P_{4441}-TFSA and N_{4441}-TFSA. Interestingly, viscosities of phosphonium ionic liquids are lower than those of the corresponding ammonium ionic liquids, whereas conductivities of phosphonium ionic liquids are higher than those of the corresponding ammonium ionic liquids. Larger phosphonium is expected to reduce electronic interaction between the cation and the counter anion. Therefore, quaternary phosphonium ionic liquids show lower viscosity and higher conductivity; these properties are suitable for the electrolyte of high-efficiency DSCs. Decomposition temperatures (T_{dec}s) of the P_{2225}-TFSA and P_{4441}-TFSA are quite high (≈380 °C) and almost have the same values the corresponding ammonium ionic liquids. The DSC devices were subjected to stability tests under visible light (AM 1.5) soaking at room temperature for 100 h. During this time period, significant degradation was not observed for the DSCs based on phosphonium and ammonium ionic liquids.

The dependence of short-circuit photocurrent and energy conversion efficiency on photo-intensity for the P_{2225}-TFSA electrolyte-based DSC device is shown in Fig. 3. J_{sc} increases as the photo-intensity becomes higher, but the relation is not linear at high intensity, suggesting limited charge transport in the electrolyte under strong photo-intensity. The energy conversion efficiencies at 7 and 40 mW cm^{-2} were 3.8% and 2.1%, respectively. Similar J_{sc} dependences on photo-intensity were observed in the other ionic liquids used in this study, whereas for the methoxyacetonitrile-based standard electrolyte, J_{sc} was almost proportional to the photo-intensity up to 100 mW cm^{-2}. The values of η at 7 mW cm^{-2} for N_{2225}-TFSA, P_{4441}-TFSA, and N_{4441}-TFSA were 2.8%, 2.6%, and 2.2%, respectively.

The viscosities of P_{2225}-TFSA and P_{4441}-TFSA are lower than those of corresponding ammonium ionic liquids, but much higher than those of common organic solvents and imidazolium-based ionic liquids. The development of "low viscous phosphonium ionic liquids" will lead to highly stable and high-performance DSC devices. Studies of lower viscous phosphonium-based ionic liquids are underway.

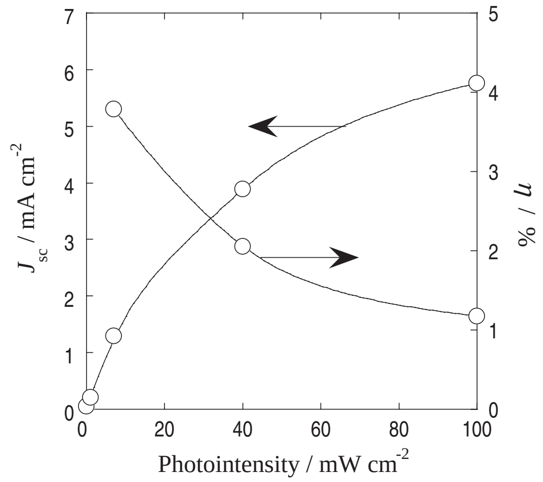

Fig. 3. Short-circuit photocurrent density and energy conversion efficiency for the P_{2225}-TFSA-electrolyte-($[I^-]$:$[I_2]$ = 10:1, $[I^-] + [I_3^-] = 1.0\,\mathrm{mol\,L^{-1}}$) based DSC device under various photointensities (AM 1.5).

In summary, the DSCs using quaternary phosphonium ionic liquids as their electrolytes have been successfully fabricated. The energy conversions of the DSC using P_{2225}-TFSA were 1.2% and 3.8% under full and low intensity sunlight illumination, respectively. Interestingly, the device performances were higher for the quaternary phosphonium ionic liquid electrolytes than those for the corresponding quaternary ammonium ionic liquids. It was found that phosphonium-based ionic liquids are promising electrolytes for the practical DSC cells.

Experimental

Materials. Quaternary phosphonium and ammonium ionic liquids were synthesized as described in previous reports.[14–16] For example, P_{2225}-TFSA was prepared by aqueous ion exchange reaction of lithium bis(trifluoromethylsulfonyl)amide with triethyl(pentyl)phosphonium bromide, which was synthesized by nucleophilic addition of triethylphosphine to 1-bromopentane. The resulting ionic liquid was washed with hexane and water, and then dried under vacuum. Triethyl(pentyl)phosphonium iodide (P_{2225}-I) was synthesized by nucleophilic addition of triethylphosphine to 1-iodopentane, and the resulting iodide was purified by recrystallization and then dried under vacuum. Other materials used were reagent grade or better and used as received.

Fabrication of DSC Devices. Photoanodes of the DSCs were prepared as follows. TiO_2 nano-particles (Solaronix D) were coated over fluorine-doped SnO_2-coated glass electrodes (Asahi glass Co., Ltd., 10.8 Ω cm^{-2}) and sintered at 450 °C for 30 min. The photoanodes (TiO_2 thickness: ca. 15 µm, area: ca. 0.7 cm × 0.7 cm) were dipped into 0.3 mmol L^{-1} *cis*-di(thiocyanato)-*N*,*N*-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid)ruthenium(II) complex (N3 dye) ethanol solution at 40 °C for several hours and treated with ethanol and acetonitrile. The N3-immobilized photoanode and platinum-deposited electrode were sandwiched together using cell holders, and electrolytes were infiltrated into the resulting cells. The photoanodes were covered by a shadow mask and the active area of the electrode was 0.283 cm^2 (radius = 0.3 cm).

Photoelectrochemical Measurement. Photocurrent–voltage characteristics were measured by using a Keithley 2400 source meter and an AM 1.5 solar simulator (Peccell PEC-L10N) furnished with a 500 W xenon lamp. The light intensity was tuned by using an ND filter. Measurements were performed at room temperature under ambient conditions. The cells were covered with UV-cutoff filter (up to 400 nm) to check the long-term stability.

Standard Organic Electrolyte Cells. We used a standard organic electrolyte cell in order to compare the DSC results with those using ionic liquid electrolytes. 0.1 $\mathrm{mol\,L^{-1}}$ LiI, 0.05 $\mathrm{mol\,L^{-1}}$ $\mathrm{I_2}$, 0.6 $\mathrm{mol\,L^{-1}}$ 1,2-dimethyl-3-propylimidazolium iodide, and 0.5 $\mathrm{mol\,L^{-1}}$ 4-*t*-butylpyridine were dissolved in methoxyacetonitrile to obtain an organic electrolyte for the standard cell.[17] Performance of the standard cell with N3 dye under AM 1.5 simulated full sunlight (100 $\mathrm{mW\,cm^{-2}}$) illumination was as follows: $J_{\mathrm{sc}} = 16.1\,\mathrm{mA\,cm^{-2}}$, $V_{\mathrm{oc}} = 721\,\mathrm{mV}$, $f\!f = 0.581$, $\eta = 6.7\%$.

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