Quaternary Phosphonium Iodides as Organic Iodide Sources for Dye-Sensitized Solar Cells

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1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention as flexible, colorful and low-cost solar cells [1-5]. The design of the DSSC is a relatively simple one, consisting of a dye-adsorbed nanoporous titanium dioxide (TiO₂) electrode, an electrolyte containing an iodide/triiodide redox couple and a platinum-coated conducting glass electrode. In order to improve the DSSC performance, variations in cell performance with different dyes, redox couples, electrolytes and electrodes have been widely studied [6-10]. The electrolyte is particularly influential component of the DSSC. For example, it is well known that lithium cations increase the short circuit current (*J*_{sc}) while decreasing the open circuit voltage (*V*_{oc}) [11]. Novel organic iodine sources are being widely investigated as effective DSSC components [12-15].

Recently, we synthesized novel quaternary phosphonium ionic liquid and used it as a nonvolatile and highly ionic conductive electrolyte for the DSSC [16-18]. Interestingly, the energy conversion efficiencies for the quaternary phosphonium ionic liquid electrolytes were higher than those for the corresponding quaternary ammonium ionic liquids. In this paper, we investigate a variety of quaternary phosphonium iodides as novel organic iodide sources for DSSCs (Fig. 1).

2. Experimental

Quaternary phosphonium iodides were synthesized as described in previous papers [16,19]. For example, triethyl(methyl)phosphonium iodide (P₂₂₂₁-I) was synthesized by nucleophilic addition of triethylphosphine to iodomethane, 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.

DSSC photoanodes were prepared as follows: TiO₂ nano-particles (Solaronix D) were coated over fluorine-doped SnO₂-coated glass electrodes (Asahi glass Co. Ltd., 10-11 Ω cm⁻²) and sintered at 450 °C for 30 min. The photoanodes (TiO₂ thickness: ca. 15 μm, area: ca. 0.7 cm × 0.7 cm) were dipped into 0.5 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-

P₂₂₂₁-I : R¹ = C₂H₅, R² = CH₃
 P₂₂₂₂-I : R¹ = C₂H₅, R² = C₂H₅
 P₂₂₂₅-I : R¹ = C₂H₅, R² = C₅H₁₁
 P₄₄₄₁-I : R¹ = C₄H₉, R² = CH₃
 P₄₄₄₄-I : R¹ = C₄H₉, R² = C₄H₉

Figure 1. Molecular structures of quaternary phosphonium iodides.

deposited electrode were sandwiched together using cell holders, and electrolytes were infiltrated into the resulting cells. The standard (conventional) electrolyte consisting of 0.1 mol l^{-1} LiI, 0.05 mol l^{-1} I_2 , 0.6 mol l^{-1} 1,2-dimethyl-3-propylimidazolium iodide and 0.5 mol l^{-1} 4-t-butylpyridine were dissolved in methoxyacetonitrile [15,16]. The photoanodes were covered by a shadow mask and the active area of the electrode was 0.283 cm^2 (radius = 0.3 cm).

Photocurrent-voltage characteristics were measured with a Keithley 2400 source meter and an AM 1.5 solar simulator (Peccell PEC-L10N) equipped with a 500 W xenon lamp. Measurements were performed at room temperature under ambient conditions.

3. Results and discussion

In order to compare this with a conventional electrolyte, we set the cation concentration to 0.7 mol l^{-1} . The photovoltaic parameters of DSSCs using various quaternary phosphonium iodide based electrolytes under full sunlight illumination (AM 1.5, 100 mW cm^{-2}) are summarized in Table 1. 4-t-butylpyridine is known to prevent the TiO_2 conduction potential from making a positive shift which is caused by adsorption on the TiO_2 surface [20]. $\text{P}_{2222}\text{-I}$ was not dissolved with a concentration of 0.7 mol l^{-1} in methoxyacetonitrile, while other quaternary phosphonium iodides were completely dissolved in the electrolyte at room temperature. For the quaternary phosphonium

Table 1. Photovoltaic parameters of DSSCs using various quaternary phosphonium and imidazolium iodides based electrolytes.^{a)}

Iodide	J_{sc} / mA cm^{-2}	V_{oc} / mV	ff	η / %
$\text{P}_{2221}\text{-I}$	16.6	661	0.60	6.6
$\text{P}_{2222}\text{-I}$	-*	-*	-*	-*
$\text{P}_{2225}\text{-I}$	15.9	665	0.57	6.0
$\text{P}_{4441}\text{-I}$	15.0	676	0.58	5.9
$\text{P}_{4444}\text{-I}$	14.9	681	0.57	5.8
DMPIIm-I	16.6	678	0.61	6.9
EMIm-I	16.1	668	0.63	6.8

a) electrolyte: 0.7 mol l^{-1} quaternary phosphonium or imidazolium iodides, 0.05 mol l^{-1} I_2 and 0.5 mol l^{-1} 4-t-butylpyridine were dissolved in methoxyacetonitrile.

* $\text{P}_{2222}\text{-I}$ was not completely dissolved in the electrolyte.

series, decreasing alkylchain length (cation size) increased the short-circuit current (J_{sc}), while the open-circuit voltage (V_{oc}) increased slightly with increasing the cation size, whereas fill factors (ff) were almost the same. The best device performance was achieved using $\text{P}_{2221}\text{-I}$ as iodide source, whose energy conversion efficiency (η) was 6.6% under full sunlight illumination. This value is comparable with or slightly lower than those of imidazolium based electrolytes.

As described above, lithium cation improves cell performances: therefore, we investigated lithium containing organic-inorganic hybrid cation based electrolytes for DSSCs. The role of the lithium cation is to increase the electron injection yield [21]. Figure 2 shows the photocurrent density-voltage characteristics for DSSC devices based on phosphonium-lithium and imidazolium-lithium hybrid (conventional) electrolytes. Interestingly, the short-circuit current for the $\text{P}_{2221}\text{-I}$ and $\text{P}_{4441}\text{-I}$ based electrolytes is higher than for the DMPIIm-I based electrolyte, while the fill factors were slightly lower than those for the DMPIIm-I. The photovoltaic parameters of the DSSCs based on various organic-inorganic

Figure 2. Photocurrent density-voltage characteristics of DSSC devices using $\text{P}_{2221}\text{-I}$ (solid line), $\text{P}_{4441}\text{-I}$ (dotted line) and DMPIIm-I (standard, dashed line) electrolytes under AM 1.5 simulated full sunlight (100 mW cm^{-2}) illumination. Each electrolyte consists of 0.1 mol l^{-1} LiI, 0.05 mol l^{-1} I_2 , 0.6 mol l^{-1} organic iodide and 0.5 mol l^{-1} 4-t-butylpyridine were dissolved in methoxyacetonitrile.

Table 2. Photovoltaic parameters of DSSCs based on organic-inorganic hybrid electrolyte containing quaternary phosphonium and imidazolium iodides.^{a)}

Organic iodide	J_{sc} / mA cm ⁻²	V_{oc} / mV	ff	η / %
P ₂₂₂₁ -I	18.5	708	0.59	7.7
P ₂₂₂₅ -I	17.5	672	0.58	6.8
P ₄₄₄₁ -I	19.2	698	0.55	7.4
P ₄₄₄₄ -I	17.1	689	0.54	6.4
DMPIm-I	18.0	683	0.61	7.5
I ^{b)}	18.0	672	0.59	7.1
II ^{c)}	18.8	699	0.59	7.8

a) electrolyte: 0.1 mol l⁻¹ LiI, 0.6 mol l⁻¹ organic iodides, 0.05 mol l⁻¹ I₂ and 0.5 mol l⁻¹ 4-t-butylpyridine were dissolved in methoxyacetonitrile. b) organic iodide: 0.3 mol l⁻¹ P₂₂₂₁-I+0.3 mol l⁻¹ DMPIm-I c) organic iodide: 0.3 mol l⁻¹ P₄₄₄₁-I+0.3 mol l⁻¹ DMPIm-I

hybrid electrolytes containing quaternary phosphonium and imidazolium iodides are summarized in Table 2. The energy conversion efficiency for the P₂₂₂₁-I and P₄₄₄₁-I based electrolytes were comparable to or slightly higher than those of the DMPIm-I based standard electrolyte. It is quite significant that the DSSC performance with easily synthesized phosphonium iodide is comparable to that with costly imidazolium iodide. The best device performance was achieved using a mixed organic iodide (II: P₄₄₄₁-I:DMPIm-I = 1:1), whose energy conversion efficiency (η) was 7.8% under full sunlight illumination. At this time, the effect of the phosphonium cation on DSSC performance cannot be understood sufficiently and is under investigation.

4. Conclusion

DSSCs using quaternary phosphonium iodides as their organic iodide sources were successfully fabricated. Interestingly, the DSSC performances for the P₂₂₂₁-I and P₄₄₄₁-I based electrolytes were comparable to or slightly better than that of the standard electrolyte. Phosphonium-based iodides are promising organic iodide sources for practical DSSC cells.

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