

Novel Imidazolium Ionic Liquids Containing Quaternary Ammonium Iodide or Secondary Amine for Dye-sensitized Solar Cell

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A new type of ionic liquid based on *N*-(3-aminepropyl)imidazolium iodide, called **IIQAI**, which consists of imidazolium and quaternary ammonium salt, and **APII-(hydroxyethyl, propyl, hexyl)** were synthesized and used as ionic liquid in dye-sensitized solar cells. **APII-hexyl** is solid, whereas **IIQAI**, **APII-(hydroxyethyl, propyl)** are viscous liquids. The synthesized ionic liquid showed relative thermal stability compared to the commercial ionic liquid of **DMII**. Among them, **IIQAI** was more stable than the other ionic liquid because of the two salt groups. **APII-hydroxyethyl**, which contains two hydroxyl groups, showed low viscosity with good flow. New types of ionic liquids were examined by ¹H-NMR spectroscopy, thermo gravimetric analysis (TGA). **IIQAI** enabled a solar energy conversion efficiency of 6.3%, which is slightly higher than that of the referenced (**DMII**, 6.2%).

Key Words : Ionic liquid, Dye-sensitized solar cell, Thermal stability, Imidazolium iodide, DSSCs

Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable attention for their easy fabrication, low cost and high conversion efficiency since Grätzel first reported dye-sensitized solar cells.^{1,2} The electrolyte, which is one of the key ingredients, provides internal electric conductivity by diffusing within the mesophase TiO₂ layer, and its properties have a considerable effect on the conversion efficiency and stability of the resulting solar cells. In recent years, ionic liquid electrolytes were developed in view of the disadvantage of organic solvent electrolyte, and have advantages, such as excellent chemical and thermal stability, non flammability, high ionic conductivity, and a wide electrochemical window.³⁻⁶ Among the onium cations with positive nitrogens, such as quaternary ammonium, pyridinium and imidazolium, those derived from the imidazolium ring are the best choice in terms of melting point and electrochemical stability. Kubo *et al.* examined the physical and physicochemical properties of a series of 1-alkyl (C₃-C₉)-3-methylimidazolium iodides.⁷ They reported that the conductivity decreased with increasing alkyl chain length, which affects the viscosity through van der Waals forces. To improve the mobility of the redox couple in the electrolyte and the photovoltaic performance, Grätzel *et al.* examined solar cells based on low-viscosity ionic liquids.^{8,9} The alkyl imidazolium cation may be absorbed on the surface of a semiconductor film to form a Helmholtz layer, which restricts the contact of triiodide and semiconductor films, to allow recombination between triiodide and the electrode in the conduction band of a semiconductor.

Unlike other ionic liquids, imidazolium-based containing secondary amine and quaternary ammonium salts group

with iodide were designed as an anionic counterpart, which provides low viscosity and possibility affects the stable Helmholtz layer on the TiO₂ surface to prepare electrolytes for DSSC. Hitoshi reported the influence of secondary amine additives in electrolytes on DSSCs.¹⁰ In our group, imidazolium ionic liquid containing secondary amine has been studied and resulted in good long term stability without side reactions.¹¹ This paper reports novel electrolytes consisting of imidazolium-based ionic liquids with a quaternary ammonium salt or secondary amine groups, as shown in Scheme 1. The effect of these imidazolium-based ionic liquids on the photovoltaic performance of DSSCs was examined. The quaternary ammonium salt containing the ionic liquid exhibited low-volatility, and amine containing ionic liquids are expected to exhibit intra- or inter-molecular hydrogen bonding interactions through its amine and imidazolium groups.¹² The photovoltaic performance and stability of the cell are discussed.

Experimental

1-(3-Aminopropyl)imidazole, 2-iodoethanol, iodomethane, iodopropane, iodoethane, and acetonitrile were purchased from Aldrich Chemical and used as received. Common reagents, such as ethylacetate, acetone and methanol, were also used without further purification.

Iodomethane (13.2 g, 0.0936 mol) in acetonitrile (10 mL) was added slowly to a solution of 1-(3-aminopropyl)imidazole (2.0 g, 0.0156 mol) in acetonitrile (20 mL) at 0 °C under a N₂ atmosphere. The reaction mixture was heated to 80 °C under reflux for 48 h. The reaction mixture was allowed to cool and the solvent was evaporated. The remaining product was washed three times with ethylacetate. The product

was evaporated under reduced pressure and dried under vacuum at 60 °C for 24 h. The viscous deep brown liquid was imidazolium iodide quaternary ammonium iodide (**IIQAI**). The synthesis of **APII-(hydroxyethyl, propyl, hexyl)** was followed by the synthesis of **IIQAI** using the same method.

The ^1H NMR spectra were recorded on a Bruker DRX (400 MHz) spectrometer using $\text{DMSO-}d_6$ as the solvent and tetramethylsilane as the internal standard. Thermo-gravimetric analysis (TGA) was performed using a Perkin-Elmer TGA7 at a heating rate of 20 °C/min under an ambient air flow of 50 mL/min.

The organic solvent based on four different structure ionic liquids was prepared by dissolving the **APII** based ammonium salts along with 0.5 M LiI, 0.05 M I_2 and 0.5 M TBP in a mixture of acetonitrile. In each electrolyte, the **IIQAI** and **APII-(hydroxyethyl, propyl, hexyl)** concentration were fixed to 0.5 M. Commercial TiO_2 paste (Ti-Nanoxide HT, Solaronix SA) was used as the TiO_2 source. A thin layer of TiO_2 paste with an area of 0.25 cm^2 was deposited on a fluorine-doped tin oxide (TCO30-8, ~8 ohm/cm^2 , Solaronix, SA) glass substrate using the doctor blade technique and sintering at 450 °C for 30 min in air. The resulting TiO_2 photoelectrodes were immersed into the dye solution (N719, Ru 535 bis-TBA, Solaronix, SA) for 24 h in the dark. The sandwich-type solar cell was assembled by sealing a Pt coated conducting glass on the photoelectrode.

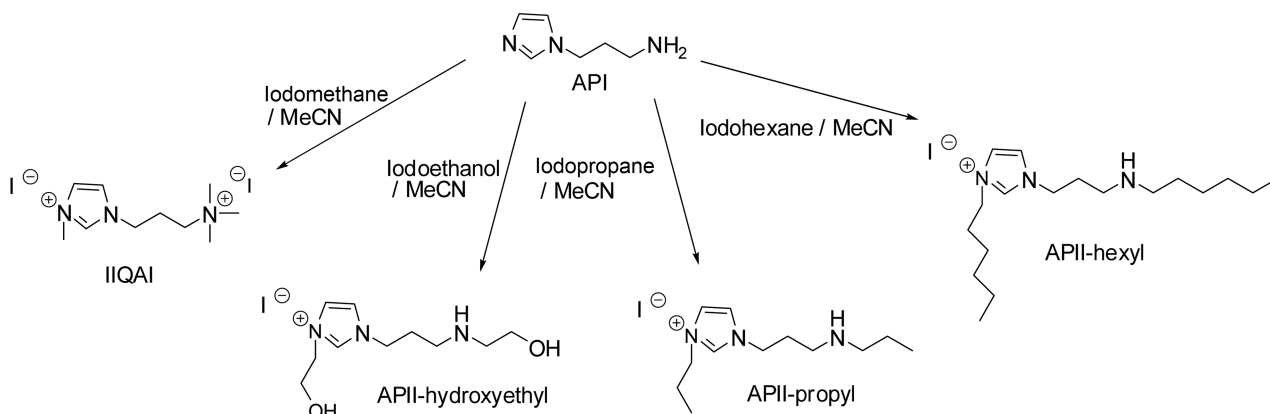
The electrochemical characterization of the electrolytes, such as cyclic voltammetry and steady-state voltammetry were performed with electrochemical workstation, CHI430A (CHI instruments, Inc., USA). A Pt disk with 3 mm in diameter and 5 μm radius Pt ultramicroelectrode (UME) were used as working electrode for cyclic voltammetry and steady-state voltammetry measurement, respectively. Ag/AgCl wire and Pt wire were used as a reference and counter electrode. A symmetric thin-layer impedance cell was constructed by two platinized FTO-glasses sandwiched with a 50 μm surlyn tape as spacer. The electrode area contacting with electrolyte was 0.1 cm^2 . The incident light intensity was adjusted to mW/cm^2 (1 sun) AM 1.5 using a 450 W Xe high power arc lamp housing (LH 151, Spectral Energy Co.). The light intensity was calibrated using a Radiometer Photometer (ILT

1400-A).

Results and Discussion

Quaternary ammonium iodide and secondary amine imidazolium iodide based ionic liquids were prepared to better understand the dependence of the molecular structure of cation and side chain in salts. **IIQAI** and **APII-(hydroxyethyl, propyl, hexyl)** were prepared as shown in Scheme 1. The chemical structures of **IIQAI**, **APII-(hydroxyethyl, propyl, hexyl)** and **API** (N-(3-aminopropyl)imidazole) were identified by ^1H -NMR, as shown in Figure 1. In **API**, the three protons between two nitrogen atoms and a carbon-carbon double bond of imidazole were observed at δ 7.61 δ 7.14-7.15, and δ 6.87-6.88 ppm, respectively. The propyl protons of H_a , H_b , and H_c of **API** were observed at δ 3.98-4.02, δ 1.70-1.77, and δ 2.44-2.50 ppm, respectively. In **IIQAI** and **APII-(hydroxyethyl, propyl, hexyl)**, the protons of imidazolium showed characteristic peaks at δ 9.14-9.32 ppm, δ 7.81-7.91 ppm, and δ 7.73-7.87 ppm because imidazole had been converted to the salt form of imidazolium, which acts as an electron-withdrawing group producing a down field shift. The propyl protons of H_a , H_b , and H_c of **IIQAI** were observed at δ 4.31-4.35, δ 2.35-2.42 and δ 3.51-3.55 ppm, respectively. The protons of H_a , H_b , and H_c of **APII-(hydroxyethyl, propyl, hexyl)** were observed at δ 4.26-4.35, δ 2.09-2.31 and δ 2.88-3.10 ppm, respectively. The propyl protons of H_a , H_b , and H_c of **IIQAI** were shifted more than that of **APII-(hydroxyethyl, propyl, hexyl)** due to ammonium iodide, which acts as an electron-withdrawing group producing a down field shift. Figure 1 shows the remaining protons. The amine and secondary amine peaks were affecting by hydrogen bonding.

The thermo-oxidative stabilities of **IIQAI** and **APII-(hydroxyethyl, propyl, hexyl)** were examined by TGA, and the results are shown in Figure 2. The TGA curves of **IIQAI** and **APII-(hydroxyethyl, propyl, hexyl)** revealed good thermal stability compared to commercial ionic liquid of **DMII**. The weight loss of **DMII** and **APII-(hydroxyethyl, propyl, hexyl)** at approximately 275 °C was due to degradation of the imidazole group. **IIQAI** showed higher thermal stability than **APII-(hydroxyethyl, propyl, hexyl)**



Scheme 1. Synthesis of **IIQAI** and **APII-(hydroxyethyl, propyl, hexyl)**.

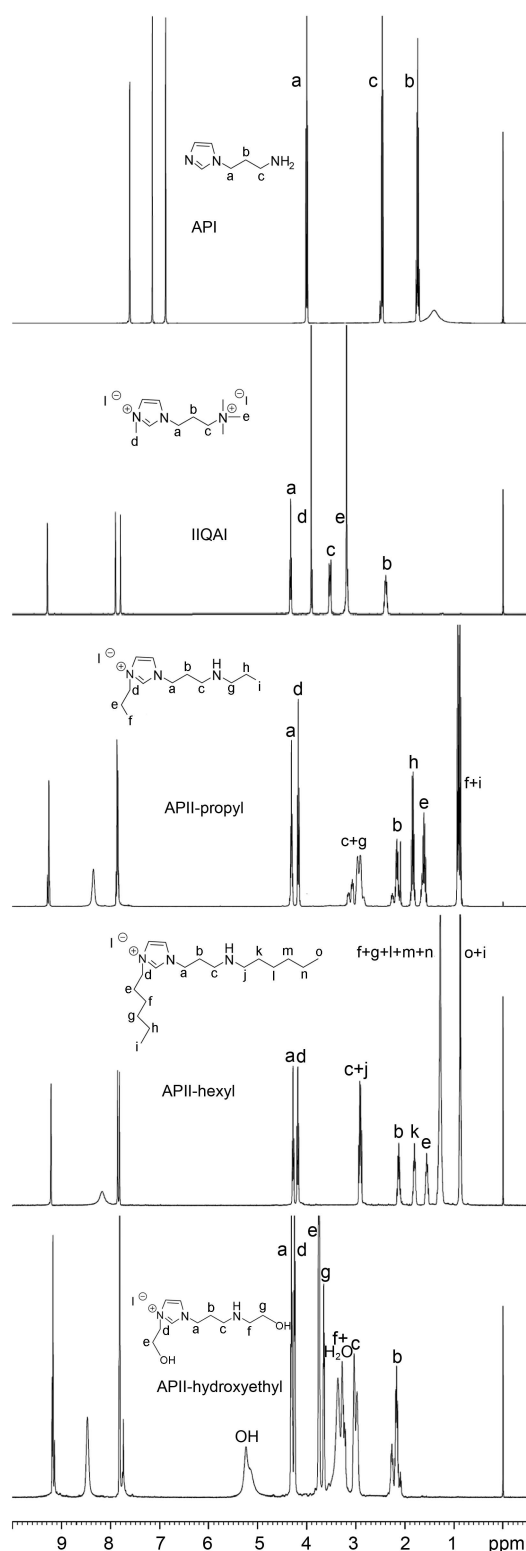


Figure 1. ^1H -NMR spectra of API, IIQAI and APII-(hydroxyethyl, propyl, hexyl).

and DMII because IIQAI had two salt groups of imidazolium iodide and quaternary ammonium iodide. The viscosity of the synthesized ionic liquid showed APII-hexyl(solid) > APII-propyl > IIQAI > APII-hydroxyethyl at 60 °C and 25 °C (Fig. 3), and was found to be dependent on the func-

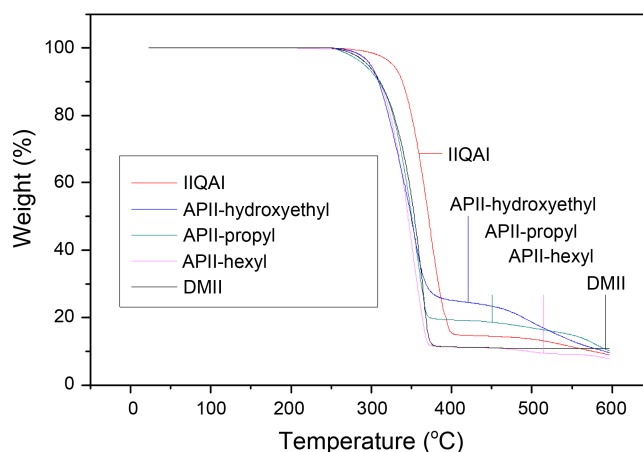


Figure 2. TGA of DMII, IIQAI and APII-(hydroxyethyl, propyl, hexyl).

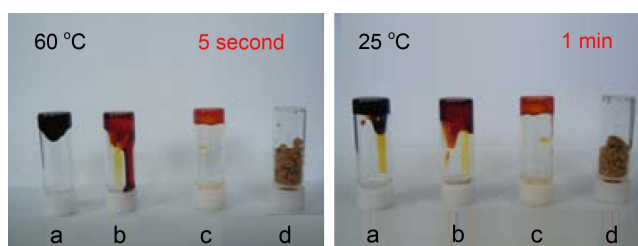


Figure 3. Viscosity of IIQAI(a), APII-hydroxyethyl(b), APII-propyl(c), APII-hexyl(d).

tional group, alkyl chain length, ammonium salt and hydroxyl group.

The diffusion coefficient of triiodide in the electrolytes was determined by measurement of acyclic voltammogram using a slow scan rate in acetonitrile at room temperature and shown in Table 1. The diffusion coefficients for the ionic liquids were found to increase in the order $(\text{DI}_3^-)_{\text{IIQAI}} > (\text{DI}_3^-)_{\text{APII-propyl}} > (\text{DI}_3^-)_{\text{APII-hexyl}} > (\text{DI}_3^-)_{\text{APII-hydroxyethyl}}$. The values of diffusion coefficient for I_3^- of ionic liquids are a little higher than that of DMII. It is observed that the values of the apparent diffusion coefficients of triiodide depend on chemical structure, and polarity of functional group linearly affects on diffusion coefficient. Figure 4 shows the photo-current density-voltage characteristics of the DSSCs based on electrolyte IIQAI and APII-(hydroxyethyl, propyl, hexyl) and open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF) and Table 1 lists the photo-

Table 1. Photo-voltaic parameters of DSSCs with different electrolytes

Electrolytes	J_{sc} (mA/cm^2)	I_{sc} (A)	V_{oc} (V)	FF (%)	η (%)
IIQA	14	2.7	0.67	67.2	6.3
APII-hydroxyethyl	12.1	2.3	0.69	57.5	4.8
APII-propyl	11.7	2.2	0.69	66.1	5.3
APII-hexyl	12	2.3	0.68	64.2	5.2
DMII	12.6	2.4	0.71	69.5	6.2

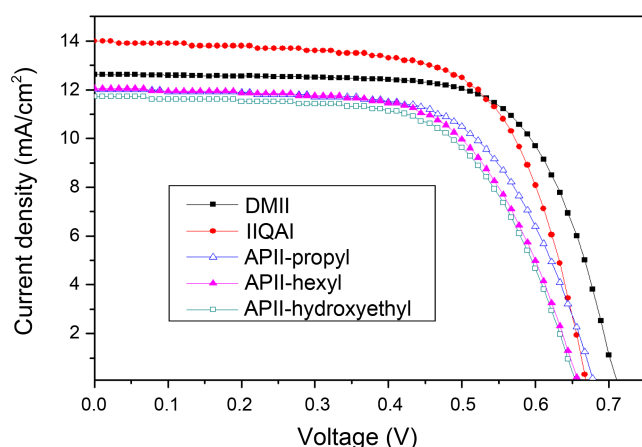


Figure 4. J-V characteristic curves of the DSSCs containing **DMII**, **IIQAI** and **APII-(hydroxyethyl, propyl, hexyl)** based electrolytes.

conversion efficiency (η %). The DSSCs with conventional liquid electrolytes, **DMII**, showed an overall efficiency of 6.2% under a 1sun condition using a home-made solar simulation system. The electrolyte containing **IIQAI** showed a maximum photo-conversion high efficiency of 6.3%, which is higher than those of **APII-(hydroxyethyl, propyl, hexyl)** (4.8%-5.3%). This suggests that the size of ionic liquid has no significant effect on the diffusion of anions when the side chain is increased. The chemical structure of the ionic liquid and the maximized degree of hydrogen bond-like inter- and/or the intra-molecular interactions *via* secondary amine and hydroxyl indicate the mainly disturbed mobility and packing of imidazolium cations on the TiO_2 surface. On the other hand, the newly synthesized **IIQAI** with highest diffusion coefficient based ionic liquid showed better thermostability and high efficiency. This indicates that the cationic imidazolium and quaternary ammonium penetrate through the dyes because the head and tail have charges, which are the driving force for the approach. Once penetration occurs, the structures of the molecules affect the packing density and surface charge. Therefore, this type of ionic liquid containing two salt groups simultaneously is an interesting chemical structure, and can be a promising material for high efficiency and stable DSSCs.

Conclusions

IIQAI and **APII-(hydroxyethyl, propyl, hexyl)** with different functional groups (quaternary ammonium, second-

ary amine and hydroxyl) were synthesized as a novel ionic liquids for dye-sensitized solar cells (DSSCs). The synthesized **IIQAI** and **APII-(hydroxyethyl, propyl)** were viscous liquids, whereas **APII-hexyl** was a solid. **IIQAI** showed relative thermal stability compared to the commercial ionic liquid of **DMII** and other ionic liquids. The diffusion coefficients for the ionic liquids were found to increase in the order $(DI_3^-)_{IIQA} > (DI_3^-)_{APII-propyl} > (DI_3^-)_{APII-hexyl} > (DI_3^-)_{APII-hydroxyethyl}$. **IIQAI** enabled a solar energy conversion efficiency of 6.3%, which is slightly higher than that of the reference **DMII** (6.2%). These results provide valuable information for further studies of a two iodide salt structure ionic liquid-based electrolytes to develop quasi-solid state DSSCs.

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