

Novel Pyridinium Iodide Containing Siloxane High Performance Electrolyte for Dye-Sensitized Solar Cell

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A new type of solid and gel-state ionics based on siloxane pyridinium iodides was synthesized and used as electrolytes in dye-sensitized solar cells. The resulting electrolytes were characterized by ^1H NMR spectroscopy, TGA and diffusion coefficient. The synthesized siloxane pyridinium iodide electrolytes have characteristics of different chain length of siloxane moieties. The ion conductivities were given 2.7-3.2 S/cm. Among the three **SiDPIs** based electrolytes, DSSC employing the **SiDPI2** gives an open circuit voltage of 0.704 V, a short-circuit current of 15.85 mA/cm² and conversion efficiency of 6.8% under light intensity of 100 mW/cm². In addition, the performance of the DSSCs showed relatively reasonable compared with the propylpyridinium iodide (PPI) electrolyte.

Key Words : Ionic liquid, Electrolyte, Dye sensitized solar cell, Pyridinium iodide, DSSCs

Introduction

The great interest in room temperature ionic liquids (RTILs) has recently rendered them one of the most attractive materials since the discovery of the first ambient temperature ionic liquid by Wier.¹ Numerous attempts to gain the fundamental understanding of the unique characteristics of the RTILs include combinations of new anions and cations to replace novel ionic liquids.²⁻⁴ In recent years, room temperature molten salts have been applied as both iodide sources and solvents for redox electrolytes in DSSCs.^{5,6} There have been many research works to improve the efficiency of dye-sensitized solar cell DSSCs using liquid electrolytes.⁵⁻⁷ Among them, especially 1-methyl-3-alkylimidazolium iodide and 1,2-dimethyl-3-alkylimidazolium iodide are mostly used for DSSCs. Recently, highest photoelectric conversion efficiency (8.2%) for the ionic liquid-based electrolyte in DSSCs has been reported.⁸ Diffusion of redox and charge carrier is an important component in electrolyte for DSSCs. Among these ionic salts, there are many species of anions, such as I⁻, BF₄⁻, PF₆⁻, (CF₃SO₂)₂N⁻, (CF₃SO₂)(CF₃CO)N⁻, TSAC etc.^{9,10} On the cationic side, molten salts incorporating imidazolium,¹¹⁻¹⁵ pyrrolidinium,¹⁶ tetraalkylammonium,^{17,18} quaternary phosphonium (QP)¹⁹ and cyclic sulfonium²⁰ cations have undergone extensive investigation. The viscosity of the ionic liquid melts should be as low as possible to avoid mass transport limitation of the photocurrent and loss of fill factor under cell operation in full sunlight. In recent years, sulfonium-based supporting electrolytes have been found to exhibit low viscosity and good electrical properties.²¹ In order to gain further understanding and extend the range of applications of pyridinium-based salts electrolytes, investigation on preparation method and properties of new class of such salts is necessary. In this study, we synthesized three pyridinium iodide salts called SiDPI1, SiDPI2 and SiDPI3 in

which siloxane groups are incorporated between pyridinium salts or sited on terminal group. In our previous studies, imidazolium iodides containing siloxane group provide low viscosity and excellent cell performance.²² Additionally, oxygens of siloxane are expected to have a complex with TiO₂ and capturing effect of cation. It can enhance the stability of the electrolytes and possibly be advantageous in transport of anionic species in the cell. Systematic studies were performed to understand the influence of these new type ionic liquid on the performance of DSSCs when they were used as a component of liquid electrolytes in organic solvent based electrolyte system. Also, the long-term stability of these ionic liquids was investigated.

Experimental

Allyl alcohol, 1,1,3,3,5,5-hexamethyltrisiloxane, thionyl chloride, poly(dimethylsiloxane) hydride terminated (average *M_n* ~580), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, pyridine, sodium iodide were purchased from Sigma-Aldrich. 1,3-Bis(chloromethyl) tetramethyldisiloxane were purchased from TCI. Common reagents, such as dichloromethane, chloroform, acetone, methanol, tetrahydrofuran were also used with or without further purification. *n*-Propylpyridinium iodide (PPI) was prepared by literature procedure.²³

Synthesis of 1,3-Bis(Iodomethyl) tetramethyldisiloxane. A solution of 1,3-bis(chloromethyl)tetramethyl-disiloxane (3 g, 12.97 mmol), sodium iodide (7.78 g, 51.89 mmol) in acetone 50 mL was refluxed at 60 °C for 24 h. The reaction mixture was allowed to cool and filtered. The filtrate was evaporated under reduced pressure and dissolved in dichloromethane. The reaction mixture was filtered. The filtrate was evaporated to remove the dichloromethane. To give 1,3-bis(iodomethyl) tetramethyldisiloxane as a yellow oil, yield 5.21 g (97%).

Synthesis of 1,3-Bis((1-methylpyridinium iodide)-3-methyl)tetramethyl-disiloxane (SiDPI1). A solution of 1,3-bis(iodomethyl) tetramethyldisiloxane (3 g, 7.24 mmol), pyridine (1.38 g, 17.38 mmol) in acetonitrile 30 mL was refluxed at 85 °C for 24 h. The reaction mixture was evaporated and washed with ethylether. The residual ethyl ether was removed by vacuum evaporation at 60 °C for 6 h to yield 3.94 g (95%).

Synthesis of (1,1,3,3,5,5-Hexamethyltrisiloxane)-1,5-dipropanol. 1,1,3,3,5,5-Hexamethyltrisiloxane (3 g, 14.39 mmol), allyl alcohol (2.01 g, 34.54 mmol) and a catalytic amount of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (1 drop) in toluene 30 mL were heated and reflux while stirring during 24 h. The reaction mixture was evaporated and then dissolved in methanol. It was passed through a plug of celite. The residual methanol was removed by vacuum evaporation to afford 4.44 g, 95% yield.

Synthesis of (1,1,3,3,5,5-Hexamethyltrisiloxane)-1,5-dipropylchloride. Thionyl chloride (10.99 g, 92.4 mmol) was carefully added to a mixture of (1,1,3,3,5,5-hexamethyltrisiloxane)-1,5-dipropanol (3 g, 9.24 mmol) and pyridine (0.07 g, 0.92 mmol) at 0 °C in an ice-water bath with constant stirring. After the addition, the mixture was permitted to warm to room temperature and then refluxed at 70 °C for 12 h. The reaction mixture was then cooled to room temperature and the excess thionyl chloride was evaporated. The residue was treated with 40 mL H₂O and the mixture was extracted with ethyl acetate (50 mL × 3). The combined ethyl extracts were washed with 100 mL saturated NaHCO₃ solution and H₂O (100 mL × 2), and then dried over anhydrous Na₂SO₄. The ethyl acetate was removed on a rotaevaporator to give (1,1,3,3,5,5-hexamethyltrisiloxane)-1,5-dipropylchloride as a brown oil, yield 3.01 g (90%).

Synthesis of (1,1,3,3,5,5-Hexamethyltrisiloxane)-1,5-dipropyl iodide. A solution of (1,1,3,3,5,5-hexamethyltrisiloxane)-1,5-dipropylchloride (3 g, 8.30 mmol), sodium iodide (4.98 g, 33.19 mmol) in acetone 50 mL was refluxed at 60 °C for 24 h. The reaction mixture was allowed to cool and filtered. The filtrate was evaporated under reduced pressure and dissolved in dichloromethane. The reaction mixture was filtered. The filtrate was evaporated to remove the dichloromethane. To give (1,1,3,3,5,5-hexamethyltrisiloxane)-1,5-dipropyl iodide as a brown oil, yield 4.38 g (97%).

Synthesis of (1,1,3,3,5,5-Hexamethyltrisiloxane)-1,5-dipropyl-(3-methylpyridinium iodide) (SiDPI2). A solution of (1,1,3,3,5,5-hexamethyltrisiloxane)-1,5-dipropyl iodide (3 g, 5.51 mmol), pyridine (1.05 g, 13.22 mmol) in acetonitrile 30 mL was refluxed at 85 °C for 24 h. The reaction mixture was evaporated and washed with ethylether. The residual ethylether was removed by vacuum evaporation at 60 °C for 6h to yield 3.68 g (95%).

Synthesis of Poly(dimethylsiloxane), Propanol Terminated. Poly(dimethylsiloxane), hydride terminated (3 g, 5.17 mmol), allyl alcohol (1.20 g, 20.69 mmol) and a catalytic amount of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (1 drop) in toluene 30 mL were heated and

reflux while stirring during 24 h. The reaction mixture was evaporated and then dissolved in methanol. It was passed through a plug of celite. The residual methanol was removed by vacuum evaporation to give 3.42 g, 95% yield.

Synthesis of Poly(Dimethylsiloxane), Propylchloride Terminated. Thionyl chloride (5.13 g, 43.09 mmol) was carefully added to a mixture of poly(dimethylsiloxane), propanol terminated (3 g, 4.31 mmol) and pyridine (0.03 g, 0.43 mmol) at 0 °C in an ice-water bath with constant stirring. After the addition, the mixture was permitted to warm to room temperature and then refluxed at 70 °C for 12 h. The reaction mixture was then cooled to room temperature and the excess thionyl chloride was evaporated. The residue was treated with 40 mL H₂O and the mixture was extracted with ethyl acetate (50 mL × 3). The combined ethyl extracts were washed with 100 mL saturated NaHCO₃ solution and H₂O (100 mL × 2), and then dried over anhydrous Na₂SO₄. The ethyl acetate was removed on a rotaevaporator to give poly(dimethylsiloxane), propylchloride terminated as a brown oil, yield 2.84 g (90%).

Synthesis of Poly(Dimethylsiloxane), Propyl iodide Terminated. A solution of poly(dimethylsiloxane), propylchloride terminated (3 g, 4.09 mmol), sodium iodide (2.45 g, 16.37 mmol) in acetone 50 mL was refluxed at 60 °C for 24 h. The reaction mixture was allowed to cool and filtered. The filtrate was evaporated under reduced and dissolved in dichloromethane. The reaction mixture was filtered. The filtrate was evaporated to remove the dichloromethane. To give poly(dimethylsiloxane), propyl iodide terminated as a brown oil, yield 3.64 g (97%).

Synthesis of Poly(dimethylsiloxane), 1-Methyl-3-propyl Pyridinium Iodide Terminated (SiDPI3). A solution of poly(dimethylsiloxane), propyl iodide terminated (3 g, 3.28 mmol), pyridine (0.62 g, 7.86 mmol) in acetonitrile 30 mL was refluxed at 85 °C for 24 h. The reaction mixture was evaporated and washed with ethylether. The residual ethylether was removed by vacuum evaporation at 60 °C for 6 h to yield 3.34 g (95%).

Preparation of Electrolytes and DSSC Fabrication. Organic solvent based solid type different electrolytes were prepared by dissolving propyl pyridinium iodide (PPI) and siloxane pyridinium iodides (SiDPI1, SiDPI2, SiDPI3) with 0.1 M guanidinium thiocyanate (GNCS), 0.05 M I₂ and 0.5 M tert-butylpyridine (TBP) in 3-methoxypropionitrile. In electrolyte the concentration of PPI was fixed as 0.6 M. Commercial titanium dioxide paste (Ti-Nanoxide HT, Solaronix SA) was used as the TiO₂ source. A thin layer of TiO₂ paste with an area of 0.1 cm² was deposited on fluorine doped tin oxide (TCO30-8, ~8 ohm/cm², Solaronix, SA) glass substrate by doctor blade technique and successive sintering at 450 °C for 30 min in air. The resulting TiO₂ photoelectrode was immersed into the dye solution (N719, Ru 535 bis-TBA, Solaronix, SA) for 24 h in dark. The sandwich-type solar cell was assembled by sealing a Pt coated conducting glass on the photoelectrode.

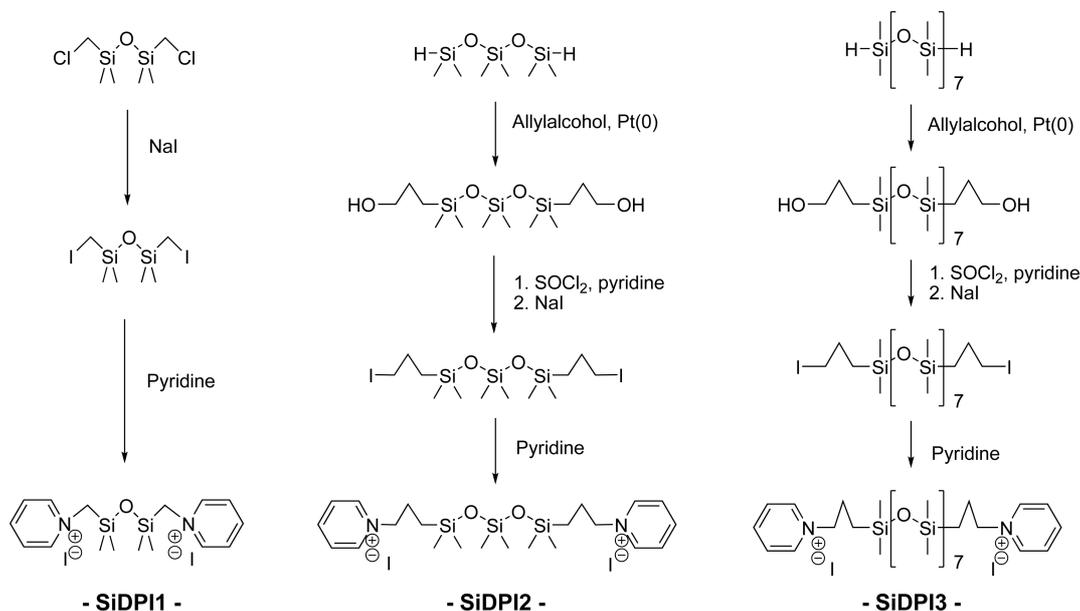
Measurements. The ¹H NMR spectra were recorded on a Bruker DRX (400 MHz) spectrometer using DMSO-*d*₆ as

the solvent and tetramethylsilane as the internal standard. And thermo-gravimetric analyses (TGA) were performed with Perkin-Elmer TGA7 at a heating rate of 20 °C/min under an ambient air flow of 50 mL/min. 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. Ion conductivity was measured with Mettler Toledo sevenmulti model S47 and electrode Inlab 731 in solution (0.05 M LiI, 0.05 M I₂, 0.05 M TBP and 0.05 M electrolyte). 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 cm². The incident light intensity was adjusted to 100 mW/cm² (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

A series of cyclic pyridinium-based electrolytes, **SiDPIs** (**SiDPI1**, **SiDPI2** and **SiDPI3**) were synthesized according to the reaction Scheme 1. Hydrosilylation reaction, which is an attractive route to form thermally and hydrolytically stable carbon silicon bond, provided convenient formation of new carbon silicon bond between allyl alcohol and hydride terminated dimethyl siloxane. This reaction was catalyzed by Pt-complex (Karstedt's catalyst) which typically proceeds to high conversions without the formation of by-products.²⁴ The chemical structures of **SiDPIs** were identified by ¹H-NMR as shown in Figure 1. The pyridine was converted to

salt form of pyridinium iodide, which acts as an electron-withdrawing group to shift down field. To confirm the chemical structure, we compared **SiDPIs** with the model compound of propyl pyridinium iodide. Interestingly, in **SiDPI1**, the proton peaks (H_a) nearby ammonium (N⁺) appeared two peaks with doublet at δ 9.12-9.13. The protons (H_b) showed triplet peaks at δ 8.61-8.65. The protons (H_c) showed triplet peaks at δ 8.17-8.20. The model compound also showed same behaviors. The protons of N⁺-CH₂-CH₂-CH₃ appeared triplet at 4.59 ppm. The protons of N⁺-CH₂-CH₂-CH₃ appeared multiplet at 1.91-1.97 ppm. The protons of N⁺-CH₂-CH₂-CH₃ appeared triplet at 0.86-0.89 ppm. In the ¹H NMR studies of **SiDPI** electrolytes, the protons of Si-CH₃ are observed at 0 ppm. The protons of pyridinium showed characteristic peaks same as model compound. Siloxanes are thermally very stable, but in the presence of strong base or strong acid, either linear or cyclic siloxanes become a mixture of cyclic and linear polysiloxanes. This means that the chemical structure of siloxane maintains original Si-O-Si bond without decomposition under severe conditions. Thermo-oxidative stabilities of **SiDPIs** (**SiDPI1**, **SiDPI2**, and **SiDPI3**) were studied using thermo gravimetric analysis (TGA) and the results were shown in Figure 2. In comparable study with **PPI**, all the synthesized compounds showed satisfactory thermal stability and their weight percent loss decreased with the increasing of silicone content. The high contents of siloxane **SiDPI3** showed 70% weight loss, whereas **PPI** almost decomposed at 330 °C. The colors and viscosities of these siloxane modified ionic liquids are different as shown in Figure 3, and solid state of **SiDPI1** with short chain length is brown color. The **SiDPI2** is shown highly viscous liquid as decreasing the siloxane chain length, showing **SiDPI2** > **SiDPI3** at 25 °C in few seconds. In general, increasing the chain length of alkyl or ethyleneoxide chains of imidazolium salts, gradually increases viscosity. We have studied linear siloxane containing mono- and bis-imida-



Scheme 1. Synthesis of **SiDPI1**, **SiDPI2** and **SiDPI3**.

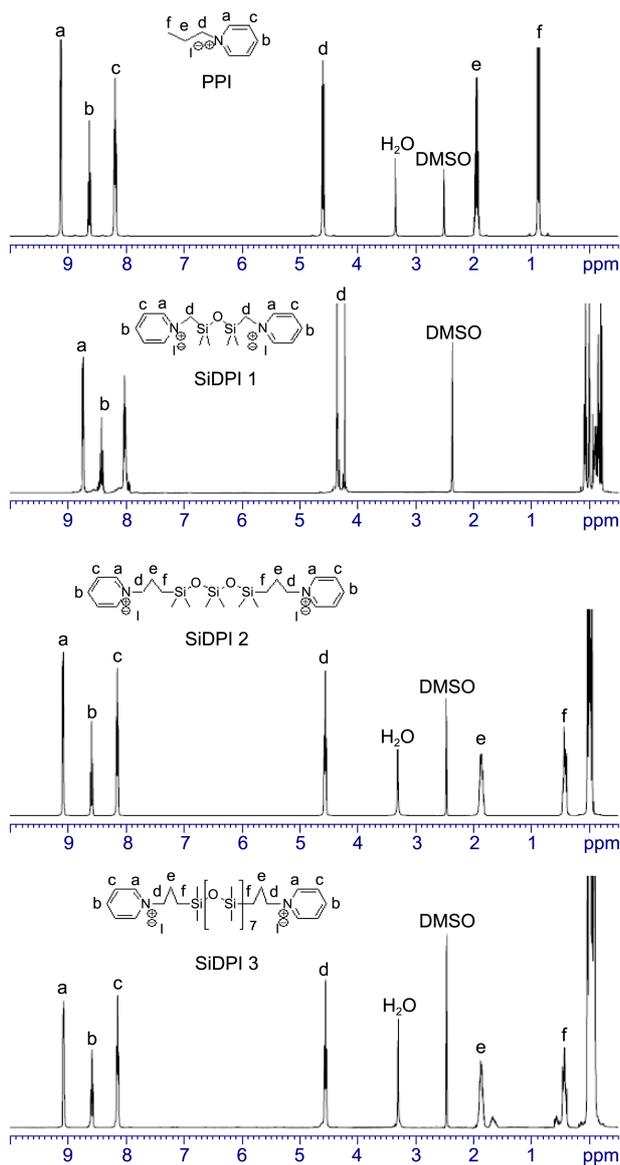


Figure 1. ^1H NMR spectra of PPI, SiDPI1, SiDPI2 and SiDPI3.

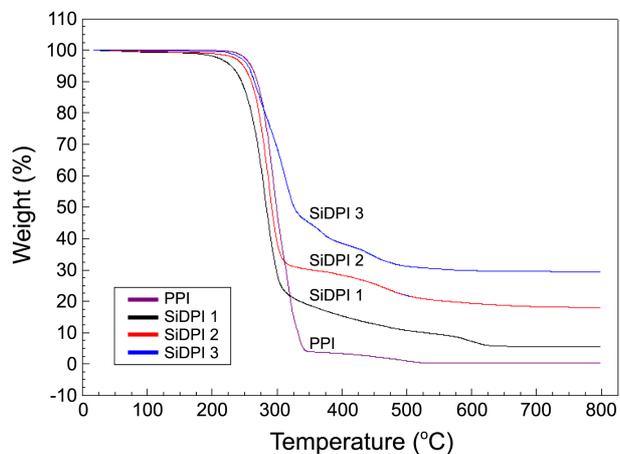


Figure 2. Thermo gravimetric analysis (TGA) curves of PPI, SiDPI1, SiDPI2 and SiDPI3.



Figure 3. Sample types of SiDPI1, SiDPI2 and SiDPI3.

zolium salts that show gel state with characteristics of excellent flexibility and low viscosity.²² However SiDPI1 electrolytes have solid because of high molecular weight and large size of ammonium element even though they have siloxane group. When siloxanes are chemically combined with hydrophilic species, such as cationic species, very interesting surfactant properties arise. The uniqueness of siloxane salts is that it is soluble in water and organic liquids, thus contributing hydrophobic as well as oleophobic properties to the molecule and hence can reduce the surface tension of both water and organic liquids. This unusual quality of siloxane salts arises from its flexibility which enables it to acquire conformations that results in close and efficient packing at various interfaces.^{24,25} The ion conductivity was measured in similar condition of DSSC cell as a function of temperature, and displayed in Figure 4. In general, the low viscosity leads to high ion mobility, thus maximizing ion conductivity. However there are some exceptions by determinant factors, concentration, solvent, mass transfer of charge carriers, and molecular weight etc..²⁶ The ion conductivities of electrolytes were increased as elevating temperature. The ion conductivity of PPI is higher than that of DMIL. Compared with SiDPI1 and SiDPI2, the ion conductivity of SiDPI3 is lower, although the viscosity is lower than those. This result shows that ion conductivity was also affected by the molecular weight of electrolyte and the

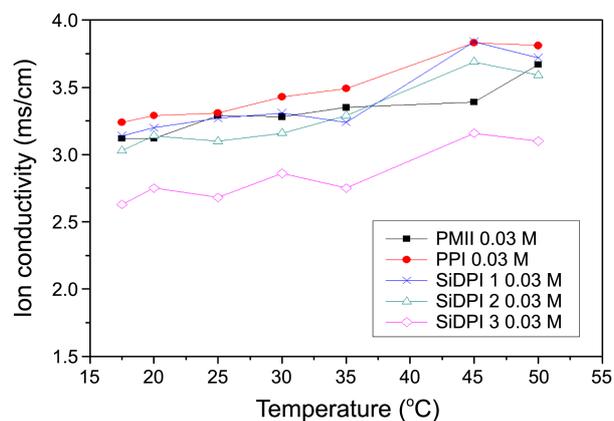


Figure 4. Ion conductivity of PPI, SiDPI1, SiDPI2 and SiDPI3.

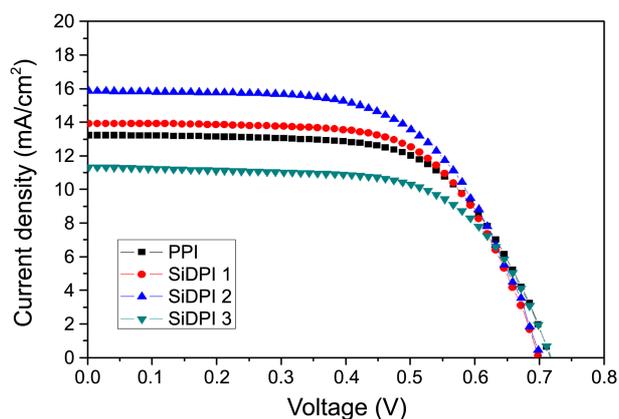


Figure 5. J–V characteristic curves of DSSCs containing PPI and SiDPIs.

chemical structure of counter cation rather than viscosity. The diffusion coefficient of triiodide in the electrolytes was determined by the cyclic voltammogram measurements using a slow scan rate in 3-methoxypropionitrile along with 40 mM SiDPIs and 50 mM I₂ at room temperature and the results are shown in Table 1.²⁷ The diffusion coefficients for I₃[−] of the SiDPI2 ($1.4 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$) has higher than PPI ($1.6 \times 10^{-8} \text{ cm}^2\text{s}^{-1}$), SiDPI1 ($1.4 \times 10^{-7} \text{ cm}^2\text{s}^{-1}$) and SiDPI3 ($5.6 \times 10^{-8} \text{ cm}^2\text{s}^{-1}$) were slightly higher than that of the reference (PPI). Diffusion coefficients of I₃[−] evidently depended on the chemical structure of pyridinium salt, anion, solubility, and molecular weight of electrolyte. This result showed that increase siloxane group in the molecules has non-polar property effect on solubility and increasing molecular weight. Thus SiDPI3 has low diffusion coefficients. Photocurrent density-voltage characteristics of the DSSCs based on new electrolytes, SiDPI1, SiDPI2, SiDPI3, and PPI as a reference electrolyte, are listed in Table 1. The DSSCs with PPI showed the efficiency of 5.9% at 1 sun condition with our home-made solar simulation system. The photo-conversions of SiDPI1 and SiDPI2 showed similar or little high efficiencies of 6.0% and 6.8% compare to that of PPI. However SiDPIs having big size and high molecular weight resulted but SiDPI3 showed the lowest efficiency of 4.7% because of the effect of low ion conductivity, although it has low viscosity. The DSSCs of SiDPI2 with high diffusion coefficient showed the highest efficiency. These phenomena could be explained that siloxane group formed on the TiO₂ surface which is the driving force for the

Table 1. Diffusion coefficient and photo-voltaic parameters of electrolytes

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)	DI ₃ [−] (cm ² s ^{−1})
PPI	0.715	13.22	62.5	5.9	1.6×10^{-8}
SiDPI1	0.705	13.93	60.9	6	1.4×10^{-7}
SiDPI2	0.703	15.85	61.2	6.8	1.4×10^{-6}
SiDPI3	0.718	11.33	58.3	4.7	5.6×10^{-8}

approach. Once the penetration occurs, then molecule structures are affecting the packing densities, thus surface charges.²⁸ When considering that lone pair electrons of siloxane group are acting as bronsted base, the increase in photocurrent density is thus unusual. Park *et al.* reported that this unusual enhancement of photocurrent along with decrease in voltage observed in the presence of thiourea is first thought to be probably due to an improved electron transport rate and/or an accelerated charge recombination rate.²⁹ These kinds of modified siloxane electrolytes are interesting chemical structure, and can be promising materials for high efficiency.

Conclusion

We successfully synthesized a series of new siloxane-containing pyridinium iodides (SiDPIs) with different siloxane chain groups to develop a novel electrolyte for DSSCs. The synthesized SiDPI1 electrolytes were brown with solid state and SiDPI2 & SiDPI3 were brown color with gel state. The SiDPI2 electrolyte showed a maximum photo-conversion efficiency of 6.8% which was higher than the 5.9% value of the reference PPI. These results provide valuable information for further studies of pyridinium iodide salts containing siloxane to develop gel-type electrolytes for the development of DSSCs.

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