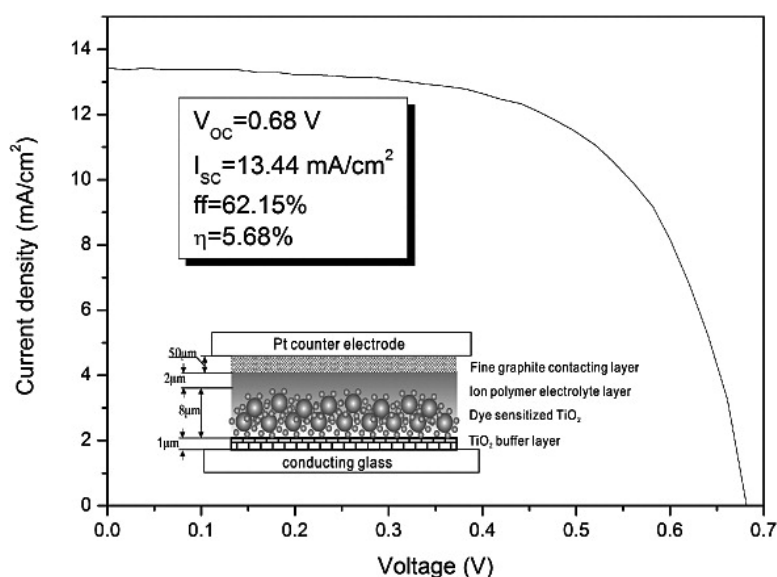Communication

An All-Solid-State Dye-Sensitized Solar Cell-Based Poly(*N*-alkyl-4-vinyl-pyridine iodide) Electrolyte with Efficiency of 5.64%

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An All-Solid-State Dye-Sensitized Solar Cell-Based Poly(N-alkyl-4-vinyl-pyridine iodide) Electrolyte with Efficiency of 5.64%

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In the past decade, considerable efforts have been devoted to the nanocrystalline dye-sensitized solar cell (DSSC) since its first successful demonstration in 1991 by M. Gratzel.[1] DSSC has been widely considered as a potential alternative to the conventional silica cells because of its low cost and simple preparation procedure.[2] On the basis of a liquid electrolyte, a DSSC with photoelectric conversion efficiency of 11% has been achieved.[2] However, the potential problems caused by the liquid electrolytes, such as the leakage and volatilization of liquid, are considered as some of the critical reasons limiting the long-term performance and practicable use of DSSCs.[3] Thus, p-type inorganic semiconductors,[4] organic hole-transport materials,[5] and/or solvent-free polymer electrolytes,[6] were used in an attempt to replace the liquid electrolytes. However, because of lower ionic conductivity and imperfect soakage of porous TiO$_2$ film for solid polymer electrolyte, it is still a great challenge to devise an all-solid-state DSSC with a total efficiency over 5%.

Poly(N-alkyl-4-vinyl-pyridine) iodide (PNR4VPI) is a solid state polymer with quaternary nitrogen atoms showing positive charges, anchoring on a polyethylene pyridine backbone, and combining I$^-$ anions with the quaternary nitrogen atom (Figure 1 shows their chemical structure). Because of the weak Lewis basicity of quaternary nitrogen atoms, the conjugation effect of the pyridine ring, and the steric hindrance of the polymer backbone, the attraction between quaternizing nitrogen atoms and I$^-$ anions is weak, resulting in the mobility of I$^-$ anions. Interestingly, by doping this solid-state polymer with iodine and N-alkyl pyridine iodide (NR′PI), the conductivity of the system can be enhance greatly. Here, we report a solid-state electrolyte with a conductivity of 6.41 mS/cm from poly(N-methyl-4-vinyl-pyridine)-doped N-methyl pyridine iodide and iodine—an efficiency of 5.64% has been achieved in an all-solid-state DSSC.

Poly(4-vinyl-pyridine) (P4VP) was synthesized by a bulk polymerization of 4-vinyl-pyridine with an initiator of azobisisobutyronitrile in nitrogen at 60 °C.[7] The various quaternizing P4VPs iodide (PNR4VPI) were prepared by adding different alkyl iodides into the methanol solution of P4VP, respectively. The quaternizing reaction was performed in a nitrogen ambience at 60 °C, finally residual quaternizing reagents were washed with diethyl ether anhydrous for several times and the products were vaccuum-dried at 50 °C for several days.

Generally, the conductivity of pure PNR4VPI is less than 10^{-3} mS/cm; this is due to the average distance between I$^-$ ions being about 0.7−0.8 nm on the PNR4VPI, which is far greater than the radius of the I$^-$ ion of 0.22 nm and the bond length of I$_2$ of 0.27 nm.[8] In this case, an effective ion transferring cannot take place for PNR4VPI.
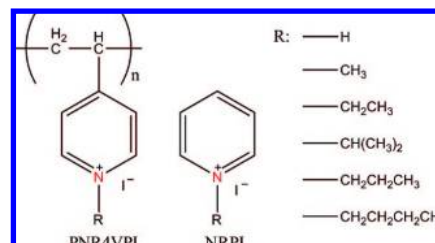

Figure 1. Chemical structure of poly(N-alkyl-4-vinyl-pyridine) iodine (PNR4VPI), and N-alkyl-4-vinylpyridine iodine(NRPI).
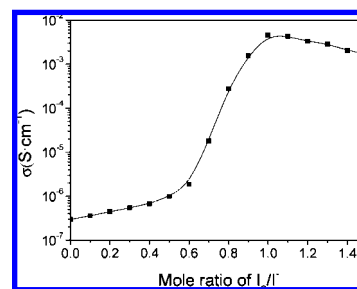

Figure 2. The influence of I$_2$ concentration on the conductivity of poly(N-methyl-4-vinyl-pyridine) iodide polymer electrolyte.

However, when iodine is introduce into the PNR4VPI system, owing to the characters of outer-shell electrons for I$^-$ ions and the labile-induced dipole for I$_2$, I$_2$ and I$^-$ combine easily to form polyiodide chains, I$_3^-$, I$_5^-$, I$_7^-$,..., I$_{2n+1}^-$, in PNR4VPI electrolyte. In the polyiodide system, the transferring effect depends on the concentration of iodine and the distance between donors (I$_{2n+1}^-$) and acceptors (I$_2$), which can be explained by a mechanism of electrical conduction in polyiodide chains via a Grotthus mechanism, a relay mechanism, in which a net transport of charge is achieved without any net transport of mass.[9−11] As shown in Figure 2, the conductivities of the polymer electrolytes increase from 10^{-3} to 4.55 mS/cm with the increase of the mole ratio of I$_2$/I$^-$ from 0 to 1. Although there is a slight decrease in conductivity when the ratio is beyond 1.0, this is because the surplus iodine reduces the efficiency of carrier transferring.

To improve the conductivity of the polymer electrolyte further, N-methyl pyridine iodide (NMPI) was added into the PNM4VPI system. As shown in Figure 3, the conductivities increase from 4.55 to 6.41 mS/cm with an increase of the mole ratio of NMPI/PNM4VPI from 0 to 0.6. This is due to the formation of polyiodide chains by NMPI combining with I$_2$. However, when the mole ratio is beyond 0.6, the conductivity decreases slightly, which maybe results from aggregates or microcrystallites from excessive NMPI blocking the transferring of carriers.

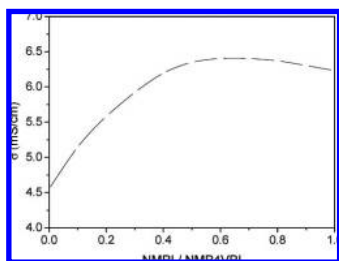[†] Huaqiao University.
[‡] Tohoku University.

Figure 3. The influence of the mole ratio of NMPI/PNM4VPI on the conductivity. The mole ratio of I_2/I^- is 1.0.

Table 1. Conductivities of PNR4VPI and NR′PI[a]

	H	methyl	ethyl	*i*-propyl	*n*-propyl	*n*-butyl
R in PNR4VPI, σ (mS·cm^{-1})[b]	6.72	4.55	3.21	2.73	2.46	1.21
R′ in NR′PI, σ (mS·cm^{-1})[c]	7.68	6.41	5.23	4.83	4.68	4.21

[a] Conductivity is measured using a four-point probe conductivity meter (RTS-9, China). [b] Conductivity measured at the mole ratio of I_2/PNM4VPI = 1.0. [c] Conductivity measured in electrolyte system with the mole ratio of NRPI/PNM4VPI at 0.6 and the mole ratio of I_2/PNM4VPI at 1.0.

Table 2. Photoelectric Properties of DSSC with TiO_2 Film Treated or Not Treated by KI.[a]

	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF	η (%)
Non-KI coated	470 ± 20	12.58 ± 0.65	0.61 ± 0.02	3.61 ± 0.26
KI coated	682 ± 30	13.44 ± 0.92	0.62 ± 0.04	5.64 ± 1.10

[a] All of values are the average of six samples.

According to the above, an optimal prescription of the polymer electrolyte should contain PNR4VPI, NR′PI and I_2. Table 1 lists the conductivities of PNR4VPI and NR′PI. The conductivity of PNR4VPI electrolyte decreases with the elongation of N-alkyl chain (R) group length. When R is H, the conductivity is 6.72 mS/cm, whereas when R is *n*-butyl, the conductivity decreases to 1.21 mS/cm. Clearly, the transferring of charger carriers is slowed because of a steric hindrance effect of the N-alkyl group; the larger R chain causes a larger hindrance effect, which results in the decrease of the conductivity with the elongation of the N-alkyl chain (R) in PNR4VPI electrolyte. A similar steric hindrance effect also occurs in NR′PI system. When the R′ in NR′PI changes from H to *n*-butyl, the conductivities of the electrolyte decrease from 7.68 to 4.21 mS/cm. Because of the thermal instability for PNH4VPI and NHPI, PNM4VPI and NMPI were chosen to constitute a solid-state polymer electrolyte with a conductivity of 6.41 mS/cm.

To improve the photoelectric performance of DSSC, a KI block layer was introduced on the surface of dye-sensitized TiO_2 film.[12,13] Compared with no KI block layer, the V_{OC} increases from 0.47 to 0.68 V, the I_{SC} increases from 12.58 to 13.44 mA/cm^2, and total effeciency increase from 3.61 to 5.64% for the DSSC with KI block layer (Table 2).

An 1 μm thick film of 5 nm-sized TiO_2 particles was first coated on the fluorine-doped SnO_2-conducting glass electrode and further coated by a 8 μm thick second layer of 20 nm-sized light-scattering anatase particles. Detailed fabrication procedures for the nanocrystalline TiO_2 photoanodes have been described elsewhere.[14] The TiO_2 film layer was sensitized by a ruthenium complex dye (N719)

from Solaronix, SA. A KI block layer was deposited on the surface of dye-sensitized TiO_2 film by immersing the film in a KI acetonitrile solution and allowing the solvent evaporate. The above-mentioned solid electrolyte ethanol solution was injected into the sandwiched cells and dried in a vacuum drying oven at 50 °C for several days. Then a fine graphite powder film (2 μm) was cast onto the surface of polymer electrolyte. Finally a Pt counter-electrode was contacted tightly with graphite layer to form a solid-state DSSC. A black mask with a 0.5×0.5 cm^2 dimension of window was covered onto the surface of the DSSC, the current−voltage characteristics of the cells were measured using a xenon arc lamp (XQ-500W, Shanghai Photoelectricity Device Company, China) with an ultraviolet filter, and the intensity was adjusted to 1 sun (100 mW/cm^2) using a calibrated c-Si solar cell. The current−voltage characteristics were obtained by applying a Keithley model 2420 digital source meter using an $I-V$ character analysis soft package for solar cell.

In summary, using PNM4VPI, NMPI, and I_2, a solid polymer electrolyte with conductivity of 6.41 mS/cm is prepared. On the basis of the solid polymer electrolyte, a conducting graphite layer, a KI block layer, and a vacuum assembling technique, we achieve an all-solid-state dye-sensitized solar cell with total photoelectric conversion efficiency of 5.64% under AM 1.5 simulated solar light intensity (100 mW/cm^2) illumination.

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