Another Role of LiI/*tert*-Butylpyridine in Room-Temperature Molten Salt Electrolytes Containing Water for Dye-Sensitized Solar Cell

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High-performance dye-sensitized solar cells having nonvolatile electrolytes are desired. We found that photovoltaic performance increased when water was added into nonvolatile organic molten salts in the presence of both LiI and *tert*-butylpyridine. We achieved 4.2% energy-conversion efficiency for the 1 cm^2 cell containing the above electrolyte (AM1.5, 100 mW/cm^2) without other volatile organic solvents.

Dye-sensitized solar cells (DSCs) have been reported to have high sun light-current conversion reaching 10% and are considered to be one of the promising candidate for next-generation solar cells.[1] DSCs contain redox species(I^-/I_3^-) and volatile organic solvents such as acetonitrile, propylene carbonate and ethylene carbonate.[2] Because of their high volatilities, solvent losses occur during long-term operations, which decreases DSC performances.

Room-temperature molten salts, such as imidazolium salts and pyridinium salts, are nonvolatile liquids with conductivity at room-temperature.[3,4] The use of these room-temperature molten salts might be a solution to the problems. However, the viscosities of the molten salts were too high to cause swift I_3^- diffusions.[5] Increases in energy-conversion efficiencies have been desired. N. Papageorgiou and his coworkers have reported that 10 to 20 wt% addition of acetonitrile to room-temperature molten salts increases diffusion rates to keep sufficient electricity under AM1.5 condition (100 mW/cm^2).[4] Volatilities of these electrolytes may decrease. However, they still contain volatile compounds. It has been reported that the viscosity of imidazolium salts decreased and the photovoltaic performance increased when more than 0.5 M of iodine was added to the molten salts.[5,6] The addition of a large amount of iodine increased Isc at the expense of Voc. Another way of decreasing the viscosity is to add water to molten salts. Additions of a small amount of water to molten salts somehow improved energy-conversion efficiencies due to the decrease in the viscosity. For example, when 5 wt% of water was added to 1-methyl-3-propylimidazolium iodine(MePrImI) containing 500 mM of iodine, the viscosity decreased from 564 mPa s (25 °C) to 53 mPa·s and the conductivity increased from 0.7 mS/cm to 5.8 mS/cm. Charge transfer resistances between electrolytes and electrodes deceased from 1.0 Ω cm^2 to a value close to 0 Ω cm^2. For comparison, in the case of a conventional electrolyte containing acetonitrile (0.5 M LiI; 0.3 M 1-hexyl-3-methylimidazolium iodide; 0.58 M *tert*-buthylpyridine; 30 mM I_2 in acetonitrile), these values are 21 mS/cm and 0.53 Ω cm^2. However, the energy-conversion efficiency started to decrease when the amount of water exceeded 5%, even though the conductivity increased monotonously with the increase in water added. We now report that photovoltaic performances increased monotonously up to at least 10 wt% of water addition when both LiI and *tert*-butylpyridine were added. The combination of LiI and *tert*-butylpyridine is quite common for conventional electrolytes containing organic solvents.[1] However, as discussed below, when water was added to the cell containing propionitrile-based-electrolytes, the energy-conversion efficiency decreased with an increase in the amount of water, which is the opposite to the phenomenon we observed in the case of molten salts. We believe that the combination of LiI and *tert*-butylpyridine has a role which is different to that in the case of conventional electrolytes.

Cis-di(thiocyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid) ruthenium(II) complex and TiO_2 past(Ti-Nanoxide) were purchased from Solaronix SA. Fluorine-doped SnO_2-layed glass plates(7–8 $\Omega/\square$)(SnO_2/F) were purchased from Nippon Sheet Glass Co., Ltd.

Liquid electrolytes consist of iodine(0.3 M) in MePrImI and a definite amount of water. The compositions of electrolytes used are summarized in Table 1. LiI was purchased from Wako Pure Chemicals Inc. *tert*-butylpyridine (*tert*-BPy) was purchased from Aldrich Corporation.

Table 1. Composition of electrolytes

Name	LiI	*tert*-BPy	I_2
A[a]	0.5 M	0.58 M	0.3 M
B[b]	0.5 M	0.58 M	0.3 M
C[a]	—	0.58 M	0.3 M
D[a]	0.5 M	—	0.3 M
E[a]	—	—	0.5 M

[a]MePrImI containing x wt% of water.
[b]MePrImI containing 20 wt% of propionitrile and x wt% of water.
The notation x was varied from 0 wt% to 10 wt%.

Dye-anchored porous TiO_2 electrodes (1 cm^2) were prepared in the way reported previously.[7]

Figure 1 shows the relationship between energy-conversion efficiencies and the amount of water added. When water was added into MePrImI (composition E), the energy-conversion efficiency did not change much. In composition E, 0.5 M of iodine was used. We also obserbed that in the case of 0.3 M iodine concentration, the energy conversion of the cell in the absence of water was almost the same as that after 10% water addition. When water was added to MePrImI containing *tert*-BPy (composition C) which is commonly employed for suppressing back-electron

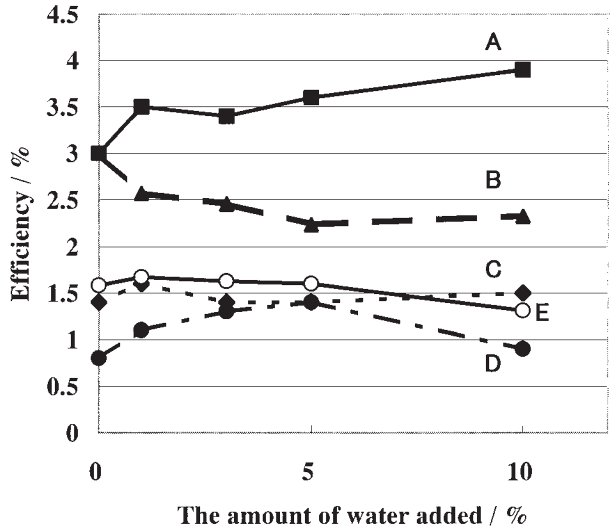

Figure 1. The relationship between energy-conversion efficiency and water content, 100 mW/cm^2, Cell area: 1 cm^2, Compositions A, B, C, D and E. See Table 1.

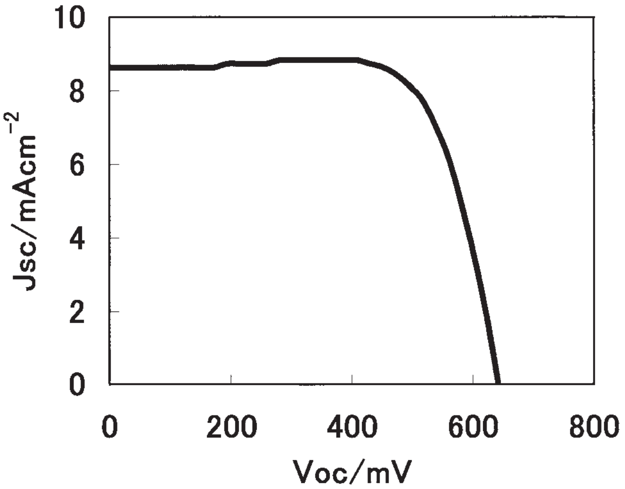

Figure 2. Photovoltaic performance for the cell containing composition A, Water content 10 wt%, 100 mW/cm^2, Cell area: 1 cm^2.

transfers and increasing Voc (open circuit voltage), efficiencies did not change. When water was added to MePrImI containing LiI (composition D) which is commonly employed for increasing Isc, the efficiency had a maximum point at 5 wt% water content. The efficiency also decreased when the water was added to the electrolyte containing MePrImI and propionitrile (80 : 20 wt%) even when they contained both Li and *tert*-BPy (composition B). We found that the efficiency increased monotonously with an increase in the amount of water up to 10 wt% when MePrImI contained both LiI and *tert*-BPy (composition A). This is unusual behavior because the addition of water did not change or decrease the efficiency for other compositions.

We observed that Voc increased from 617 mV to 665 mV when the water content increased from 0% to 10% for composition A, but the Voc was almost constant for composition C and composition D. When 25% of water was added, the relative energy conversion decreased to 70%, compared to that in the case of 10% water addition. We tried to add 50% and 75% of water. However, phase separation was observed. Water layer separated from MePrImI containing iodine. We do not have any evidence capable of explaining the phenomena fully. The phenomena might be explained by the close interactions among LiI, *tert*-BPy and water. Further experiments are under way to elucidate the mechanism. Figure 2 shows photovoltaic performances obtained for this cell. 4.2% of the energy-conversion efficiency was observed for 1 cm^2 cells. The presence of water in dye-sensitized solar cells toward stabilities is still controversial. We observed no serious decreases in their photovoltaic performances after they were stored for one month at room temperature.

In conclusion, we found that energy-conversion efficiencies increased monotonously with an increase in the amount of water up to at least 10 wt% in the presence of both LiI and *tert*-butylpyridine. We achieved 4.2% energy-conversion efficiency for a 1 cm^2 cell without other volatile organic solvents beside *tert*-butylpyridine which should be replaced with other nonvolatile aromatic amines. These results provide an important suggestion as to how high-performance photovoltaic cells that do not contain volatile organic solvents might be realized.

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