Anomalous Increase in Photocurrent Density for Quasi-solid Dye Sensitized Solar Cells by Addition of Tetra(bromomethyl)benzene

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Anomalous phenomena on gel electrolytes for quasi-dye sensitized solar cells are reported. Performances for gel electrolytes usually decrease with an increase in the amount of gelators. When tetra(bromomethyl)benzene providing three dimensional ionomer gel electrolytes is used, photocurrents increase with an increase in the amount of the gelator. This may be explained partially by decrease in interfacial resistances between gel electrolytes and electrodes.

Dye sensitized solar cells (DSCs) composed of nano-size-titanium oxide particles covered with organic dyes have been reported to exhibit high sun light-current conversion reaching 10% and one of the promising candidates for the next generation of solar cells.[1] The DSC needs liquid electrolytes containing redox species (I^-/I_3^-) and volatile organic solvents such as acetonitrile, propylene carbonate and ethylene carbonate. Among these organic solvents, nitrile compounds, such as acetonitrile and propionitrile, have been reported to exhibit best performances because of the low viscosity providing high diffusion constants of the redox species and low interfacial resistances between electrolytes and electrodes.[2] However, it has been reported that because of their high volatilities, solvent losses occur during long-term operations, resulting in decrease in DSC performances. Another problem includes solvent leakage when this is broken.

Room temperature molten salts, such as imidazolium salts and pyridinium salts, are non-volatile liquids with conductivity at room temperature.[3,4] The use of these room temperature molten salts might be one of the solutions toward the problems. However, the viscosities of the molten salts were too high to cause swift I_3^- diffusions.[5] Papageorgiou and his coworkers have reported that 10 to 20% addition of acetonitrile to room-temperature molten salts increases the diffusion rate to keep enough electricity under AM1.5 condition (100 mW/cm^2).[5]

Another approach to solve these problems is solidifications of electrolytes. Replacement of liquid electrolytes with all-solid polymer electrolytes would solve the problems concerning solvent volatilities. However, the all-solid polymer electrolytes have not exhibited high photo-voltaic performances probably because ionic diffusions are retarded.[6] The combination of gel electrolytes and room temperature molten salts containing a small amount of organic solvents should be a candidate to retard the solvent volatility and prevent solvent leakages when cells are broken. We have already reported chemically cross-linked gel electrolytes for DSCs, where cross-linked ionomers are used as gelators.[7] Commonly, gel electrolyte performances decrease with an increase the amount of gelators because gelators are electrochemically inactive.[8] We now report anomalous phenomena that photovoltaic performances increase with an increase in the amount of tetra(bromomethyl)benzene, one component of gelators.

cis-Di(thiocyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid) ruthenium(II) complex and TiO_2 paste(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 (0.1 M) in methylpropylimidazoliumiodide(80 wt%) and propionitrile(20 wt%). The compositions of electrolytes used are summarized in Table 1. Polyvinylpyridine (PVP) (Mw,160,000) and tetra(bromomethyl)-benzene (TBMB) were purchased from Aldrich Corporation.

Table 1. Gelator composition in liquid electrolytes

Name	PVP[a]	TBMB[b]
EL1	1.5 wt%	1.5 wt%
EL2	1.5 wt%	3.0 wt%
EL3	1.5 wt%	4.5 wt%

Electrolyte composition:
methylpropylimidazoliumiodide:
propionitrile=80 : 20 (wt%), Iodine 100 mM.
Figures in the Table show weight% toward the electrolyte.
[a]PVP: Polyvinylpyridine [b]TBMB: tetra(bromomethyl)benzene.

Dye-anchored porous TiO_2 electrodes (1 cm^2) were prepared using *cis*-di(thiocyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid) ruthenium(II) complex, TiO_2 past and a fluorine-doped SnO_2-layered glass plate in the method reported previously.[1] Counter electrodes were prepared by sputtering Pt on SnO_2/F layered glass plates (Nippon Sheet Glass Co. Ltd). A plastic sheet (Surlyn, Dupont. Co. Ltd.) was inserted between the TiO_2 and the counter electrodes as the spacer. The gap was controlled to be about 40 μm. Gel electrolyte precursors (Pre-GE) summarized in Table 1 were injected into the space between two electrode plates at room temperature. After the electrolytes were injected into cells, the cell was baked at 80 °C for 5 min, during which gelation occurred. The gelation is brought about by reacting PVP with TBMB to make crosslinked ionomers. Finally, the cell was sealed with epoxy resins. Interfacial resistances were monitored in the method described in the literature.[2,5] The symmetrical cells sandwiched with two sputtered Pt electrodes fabricated on SnO_2/F glasses, were used for the measurement. The interfacial resistance between sputtered Pt electrodes and gel electrolytes was estimated by using a simple Cole-Cole plot. Impedance spectra were recorded over frequency ranges of 1 to 100 MHz with an AC amplitude of 10 mV using Solartron SI1287 Electrochemical and Solartron 1255B Frequency Response Analyzer (Toyo Technical Research Co. Ltd.).

Treatment of Pt electrodes was carried out in the following methods. The Pt electrodes were dipped in 1 wt% of TBMB solution in acetone for 1 night. Then the electrodes were rinsed with acetone and dried at room temperature. Photo-electrochemical measurements were performed using solar simulator (WXS-R50S-1.5, Maki Manufacturing Co. Ltd.) furnished with a Xenon lamp (AM1.5, 100 mW/cm^2). The light intensity was monitored with a polysilicon illuminometer standardized by Japan Quality Assurance Organization (JQA). Figure 1 shows the relationship between photocurrents and voltages. The photocurrent increased from 6 mA/cm^2 to 10 mA/cm^2 when the amount of TBMB increased from 1.5% to 4.5%. FF (fill factor) also increased with an increase in the amount of TBMB from 0.43 to 0.62. However, Voc (open circuit voltage) did not changed. This is surprising result because it is well known that the electrolyte performances such as ionic conductivities and interfacial resistances decreased with an increase in the amount of gelators.[8]

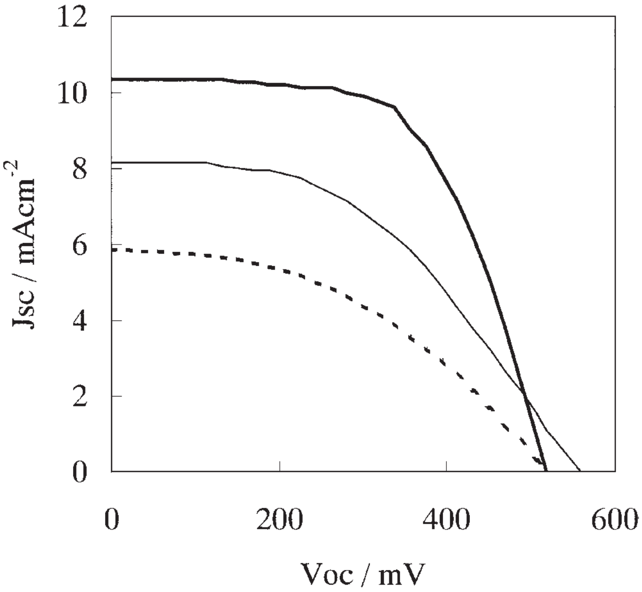

Figure 1. The relationship between photocurrents and voltages of DSCs using LE1 (dotted line), LE2 (solid Line) and LE3 (bold solid line) under AM1.5 condition (100 mW/cm^2). Cell area: 1 cm^2.

The increase in the photocurrent was not observed when other alkyl dibromide, such as dibromohexane and dibromodecane as the component for gelators. This phenomenon was observed specifically for TBMB gels. The interfacial resistance between electrolytes and Pt-electrodes treated with TBMB was found to decrease from 5.4 Ωcm^2 to 3.7 Ωcm^2 after the electrode was treated with TBMB. It seems that the change is not very large to explain the large increase in the photocurrents. However, this is at least associated with the increases in the photocurrent density and fill factors. We now suspect that the TBMB molecules may be bonded on the surface of Pt electrodes directly, which improves electron transfers between electrolytes and electrodes. In case of gel electrolytes, TBMB also may play roles to connect gel electrolytes with Pt electrodes, resulting in improving interfacial properties. If the interfacial resistance between TiO_2 (or SnO_2/F) and I_3^- also decreases on the addition of TBMB, back electron shifts from TiO_2 (or SnO_2/F) and I_3^- are also accelerated resulting in the decrease in the photo-voltaic performance. However, the decrease has not been observed. It has been reported that imidazolium salts are adsorbed on the surface of TiO_2 (or SnO_2/F), which retards the back electron transfers.[9] Because of the strong adsorption of the imidazolium salts, the effect on the TBMB addition would not be observed remarkably at TiO_2 electrodes. Considering the fact that the amount of TBMB is larger than that of PVP, we can not deny the possibility that the TBMB acts as plasticizers in gel electrolytes. The anomalous increase in the photocurrent was not observed for 1,6-dibromohexane. Therefore, Br ions formed by the reaction of PVP and TBMB seem to have nothing to do with the photocurrent increase. Further experiments are under way to clarify the effect of TBMB. In conclusion, we found that the addition of TBMB, one of gelator components, particularly increased photocurrent densities and fill factors. This is an anomalous phenomenon because commonly the gel electrolytes performance decreased with an increase in the amount of gelators. This is likely to be brought about partially by improving interfacial properties between electrolytes and electrodes. This is an important finding to prepare high-efficient-quasi-solid dye sensitized solar cells.

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