Ionic liquid crystal as a hole transport layer of dye-sensitized solar cells

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Use of a new ionic liquid crystal, 1-dodecyl-3-methylimidazolium iodide, and iodine as an electrolyte of dye-sensitized solar cells leads to a high short circuit photocurrent density and a high light-to-electricity conversion efficiency, due to a self-assembled structure of the imidazolium cations, resulting in high conductivity of the electrolyte.

Dye-sensitized solar cells (DSSC), constructed by using dye molecules, nanocrystalline metal oxides and liquid electrolytes, have attractive features in terms of the high light-to-electricity conversion efficiency, and the low production cost and energy.[1] The electrolytes, usually composed of an I^-/I_3^- redox couple in organic solvents, are sealed between two electrodes. These organic solvents cause a serious problem of low durability due to evaporation.[2] It has been reported that DSSC using ionic liquids as a non-volatile solvent achieves high temperature stability.[3,4] However, the conversion efficiency of the cells using ionic liquids is lower than that using organic solvents, because the high viscosity of the ionic liquids retards the physical diffusion of I^- and I_3^-. Many attempts to reduce the viscosity have not yet been successful.[5] For enhancing the conductivity of ionic liquids leading to the high light-to-electricity conversion efficiency of DSSC, it seems to be necessary to arrange a pathway for fast charge transport.

Previously, we reported that the charge transport rate at high concentration of an I^-/I_3^- redox couple in ionic liquids can be attributed to the exchange reaction of $I^- + I_3^- \rightarrow I_3^- + I^-$.[4,6] For enhancing the short circuit photocurrent density (J_{SC}) of DSSC using ionic liquids with a high concentration of an I^-/I_3^- redox couple, the exchange reaction in the ionic liquids needs to be promoted. In this study, we report a new strategy for enhancing the conductivity of ionic liquid electrolytes; employing an ionic liquid crystal (ILC) as a constituent of an electrolyte, which forms a self-assembled structure and promotes the exchange reaction by the locally increased concentrations of I^- and I_3^-. We have selected 1-dodecyl-3-methylimidazolium iodide (C_{12}MImI) as an ILC. This provides a self-assembled structure of the imidazolium cations like a solid, while maintaining the molecular dynamics like a liquid. The ILC with the smectic A phase (S_A) has a bilayer structure of interdigitated alkyl chains of the imidazolium cations, and I^- and I_3^- would be localized between the S_A layers. The locally high concentration would promote the exchange reaction. So, the ILC with the S_A phase would be suitable for the electrolyte of DSSC when aiming at the high light-to-electricity conversion efficiency.

A few examples of the ILC with the S_A phase, such as imidazolium salts consisting of cations with alkyl chains of C_{12}–C_{18} and anions of hexafluorophosphate or bromide, have been reported.[7,8] Iodide is indispensable in a DSSC electrolyte, because the I^-/I_3^- redox couple functions as a hole transport agent. However, an imidazolium salt with iodide as the counter anion has not been reported to be an ILC with a S_A phase. Here, we show for the first time that imidazolium iodides with alkyl chains longer than C_{12} exhibit a S_A phase and that the liquid crystalline nature is preferable in terms of the hole transport layer in DSSC.

Imidazolium iodides with long alkyl chains were synthesized by the quaternization reaction of 1-methylimidazole with an equimolar amount of the corresponding alkyl iodide for 72 h under N_2 atmosphere at room temperature. The products were washed with *n*-hexane to remove the remaining starting materials and dried under vacuum at 40 °C for 4 h, and finally identified by ^{1}H NMR in $CDCl_3$ and differential scanning calorimetry (DSC). Imidazolium iodides with alkyl chains longer than C_{12} showed a liquid crystalline phase. C_{12}MImI showed the lowest melting point and viscosity among them and these properties were suitable for the hole transport layer in DSSC. In this study, we selected C_{12}MImI and applied it with 0.65 M iodine (C_{12}MImI/I_2) as the hole transport layer in DSSC. We have compared the properties of C_{12}MImI/I_2 with an ionic liquid electrolyte; 1-undecyl-3-methylimidazolium iodide with 0.65 M iodine (C_{11}MImI/I_2).

C_{12}MImI showed a phase transition from a liquid to a liquid crystal at 80 °C, although C_{11}MImI did not show a liquid crystalline phase. The ionic liquid crystalline phase of C_{12}MImI was confirmed by polarized optical microscopy (POM). The characteristic focal conic domains observed during the cooling process suggested that the liquid crystalline phase of C_{12}MImI was a S_A phase.[7]

Photoelectrochemical cells were fabricated as previously described.[9] C_{11}MImI/I_2 and C_{12}MImI/I_2 were used as the hole transport layer, respectively. C_{12}MImI/I_2 maintained the S_A phase ranging from 27 to 45 °C on heating. On the other hand, C_{11}MImI/I_2 showed a liquid phase above 37 °C.

The light-to-electricity conversion efficiencies of DSSC using C_{12}MImI/I_2 and C_{11}MImI/I_2 were evaluated at 40 °C under AM 1.5 irradiation from a solar simulator, adaptable for amorphous silicon solar cells according to the Japanese Industrial Standard.[10] Each value for cell performance was taken as an average of at least 3 samples.

Fig. 1 shows photocurrent–voltage curves of the DSSC using C_{12}MImI/I_2 and C_{11}MImI/I_2. J_{SC} of the DSSC using C_{12}MImI/I_2 was higher than that using C_{11}MImI/I_2, while the open circuit voltage (V_{OC}) and fill factor (FF) were the almost same values as

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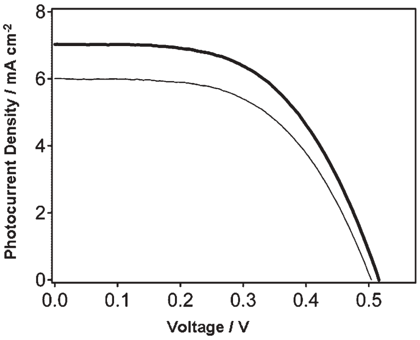

Fig. 1 Photocurrent–voltage curves of the cells using $C_{12}MImI/I_2$ (bold solid curve) and $C_{11}MImI/I_2$ (solid curve) under AM 1.5 irradiation.

for $C_{11}MImI/I_2$. This result suggests that the higher conductivity of $C_{12}MImI/I_2$ than $C_{11}MImI/I_2$ could lead to a high J_{SC}.[11,12]

To examine the conductivities of $C_{12}MImI/I_2$ and $C_{11}MImI/I_2$, the diffusion-limited currents (I_{lim}) corresponding to the reaction of $I_3^- + 2e^- \rightarrow 3I^-$ were measured. The measurements were carried out at 40 °C by using a microelectrode and the diffusion coefficients (D) of I_3^- were calculated using the values of I_{lim} as previously described.[6] According to this study, the D value calculated from I_{lim} intrinsically includes not only the simple physical diffusion coefficient but also the diffusion coefficient based on the exchange reaction.

The observed D value of $C_{12}MImI/I_2$ (4.2×10^{-8} cm^2 s^{-1}) was 1.3 times as large as that of $C_{11}MImI/I_2$ (3.2×10^{-8} cm^2 s^{-1}), while the viscosity of $C_{12}MImI/I_2$ was 2.5 times larger than that of $C_{11}MImI/I_2$. The simple physical diffusion coefficient of $C_{12}MImI/I_2$ should be smaller than $C_{11}MImI/I_2$. This result would lead to the idea that the diffusion coefficient based on the exchange reaction is increased in $C_{12}MImI/I_2$. It has been reported that anisotropic long-range conductive pathways between the S_A layers are formed in liquid crystals with a S_A phase.[13] In $C_{12}MImI/I_2$, these pathways should be formed, and I^- and I_3^- should be located between the S_A layers consisting of the imidazolium cations. If a locally high concentration of I^- and I_3^- is achieved in the pathways, the exchange reaction should be promoted in $C_{12}MImI/I_2$, since the diffusion coefficient value based on the exchange reaction is proportional to the concentrations of I^- and I_3^-. So, $C_{12}MImI/I_2$ could show a higher D value than $C_{11}MImI/I_2$ in which the cations should exist at random.

To prove that the exchange reaction was promoted in the pathways between the S_A layers of $C_{12}MImI/I_2$, we measured the ionic conductivities along the direction parallel ($\sigma_{i\parallel}$) and perpendicular ($\sigma_{i\perp}$) to the S_A layer plane[13] at temperatures ranging from 32.5 to 57.5 °C. A glass plate with comb-shaped platinum electrodes (cell A) and a pair of indium tin oxide (ITO) electrodes (cell B) were employed for the measurements of $\sigma_{i\parallel}$ and $\sigma_{i\perp}$, respectively. The conoscopic image at 40 °C for $C_{12}MImI/I_2$ revealed that the self-assemblies of the cations formed a homeotropic alignment in the S_A phase on the glass surface.

Fig. 2 shows anisotropic ionic conductivities of $C_{12}MImI/I_2$ and isotropic ionic conductivities of $C_{11}MImI/I_2$ as a function of temperature. It was reported that the ionic conductivities of isotropic ionic liquids gradually increased with the increase in temperature as shown in the insert of Fig. 2.[14] In contrast, for $C_{12}MImI/I_2$, the discontinuous changes of ionic conductivities were observed. The ionic conductivities parallel ($\sigma_{i\parallel}$) to the S_A layer of $C_{12}MImI/I_2$ decreased and those perpendicular ($\sigma_{i\perp}$) increased at 45 °C on heating. When the liquid crystalline phase-order disappeared above the phase transition temperature, the ionic conductivities measured in both cell A and cell B were on the same line within the limits of error. Taking into account that $C_{11}MImI/I_2$ did not show any discontinuous changes in $\sigma_{i\parallel}$ and $\sigma_{i\perp}$ over the whole temperature range, the discontinuous changes of $C_{12}MImI/I_2$ should be attributed to the conductive pathways formed between the S_A layers. The observed $\sigma_{i\parallel}$ values of $C_{12}MImI/I_2$ below 45 °C, which showed ionic conductivities along the direction of the conductive pathways, were enhanced because the exchange reaction would be promoted at the conductive pathways.

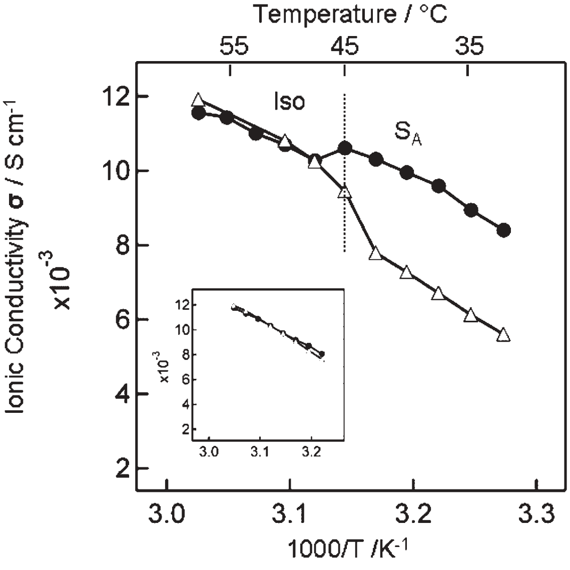

Fig. 2 Ionic conductivities for the samples of $C_{12}MImI/I_2$ and $C_{11}MImI/I_2$ (insert) along with the direction parallel $\sigma_{i\parallel}$ (filled circles) and perpendicular $\sigma_{i\perp}$ (open triangles) to the S_A layer plane of the homeotropically aligned ionic liquid crystal.

In the DSSC using $C_{12}MImI/I_2$, although the long-range order of ILC was not necessarily achieved in the mesoporous TiO_2 electrode, the localization of I^- and I_3^- between the S_A layers of each domain should result in the promotion of the exchange reaction in a hole transport layer and the enhancement in J_{SC}.

In conclusion, we have demonstrated a new strategy for enhancing the conductivity of the ionic liquid electrolytes containing an I^-/I_3^- redox couple. This strategy is based on the promotion of the exchange reaction between I^- and I_3^- by the locally increased concentrations of I^- and I_3^-. As a means of demonstrating this strategy, a new ionic liquid crystalline $C_{12}MImI/I_2$ with a self-assembled structure of the imidazolium cations was introduced. $C_{12}MImI/I_2$ showed a high ionic conductivity in spite of its high viscosity. The ionic liquid crystalline hole transport layer ($C_{12}MImI/I_2$) was applied to DSSC, which showed a higher J_{SC} and a higher light-to-electricity conversion efficiency than that using the ionic liquid hole transport layer ($C_{11}MImI/I_2$).

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