Anomaly of charge transport of an iodide/tri-iodide redox couple in an ionic liquid and its importance in dye-sensitized solar cells

Ryuji Kawano and Masayoshi Watanabe*

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Fast charge transport based on the exchange reaction of an I^-/I_3^- redox couple, which has been observed in ionic liquids due to their high ionic strength but not in molecular liquids, contributes to the high performance of dye-sensitized solar cells using the ionic liquids in spite of their high viscosity.

Ionic liquids have been recognized as an ideal electrolyte for electrochemical devices owing to their unique properties, such as non-volatility, non-flammability, high ionic conductivity and gel-forming property with polymers.[1] Examples include lithium batteries,[2] fuel cells,[3] double-layer capacitors,[4] actuators,[5] and dye-sensitized solar cells (DSSCs).[6] However, the high viscosity of ionic liquids is a serious drawback when they are used as mass-transporting media. An I^-/I_3^- redox couple has played an important role for charge transport in DSSCs.[7] It was reported that the Grotthuss-like ion transport in 1-hexyl-3-methylimidazolium iodide (HMImI) contributed to the charge transport of an I^-/I_3^- redox couple.[6a] Recently, we succeeded in differentiating the contributions of physical diffusion (D_{phys}) and exchange-reaction-based diffusion (D_{ex}) of an I^-/I_3^- redox couple to the electron transport processes in 1-ethyl-3-methylimidazolium bis-(trifluoromethane sulfonyl)imide (EMImTFSI) by using an ultra-microelectrode technique.[8] It has been found that D_{ex} dominates over the whole charge transport processes at high I^-/I_3^- redox couple concentrations. This seems to be a reason for the fast charge transport in the ionic liquids, in spite of their high viscosity. We have also investigated structural effects on the performances by adopting a wide variety of ionic liquids containing the redox couple as the electrolytes of DSSCs.[9] Consequently, it was revealed that a photo-cell with the electrolyte using an ionic liquid could achieve more than 90% of the photo-energy conversion efficiency of a cell with a low viscous organic solvent. However, whether or not the fast charge transport based on exchange reactions is specific in ionic liquids has not been elucidated. The rate-constant for the exchange reaction between I^- and I_3^-, calculated from electrochemical measurements, was close to the value obtained on the assumption of a diffusion-controlled reaction. The exchange-reaction-based diffusion in ionic liquids was larger than the physical diffusion when the redox couple concentration was high and $[I^-]$ and $[I_3^-]$ were comparable.[8] In this study, we report a comparison of the charge transport property in an ionic liquid and in a viscous molecular liquid.

An ionic liquid, EMImTFSI, was used since it is hydrophobic and is easily prepared in high purity.[10] An I^-/I_3^- redox couple should be dissolved at high concentration in a molecular liquid, because the exchange reaction occurs at high concentration of the redox couple. Further, viscosity of the molecular liquid should be similar to that of the ionic liquid for a proper comparison, since a high D_{phys} may obscure the contribution of D_{ex} to the charge transport process. What fulfils the requirements is rather restricted. Fortunately, polyethylene glycol dimethylether (PEGDE, nominal molecular weight of 500) adequately met the requirements and was used in this study. 1-Ethyl-3-methylimidazolium iodide (EMImI) and I_2 were dissolved in EMImTFSI and PEGDE as a redox couple in a glove box, and their total concentrations and the molar ratios were changed. It was assumed that I^- and I_2 immediately formed I_3^- in these liquids. The viscosity of EMImTFSI and PEGDE is 27 mPa s and 19 mPa s at 30 °C, respectively. The viscosities were similar at each temperature. An ultra-microelectrode technique was employed for the electrochemical measurements in order to simplify determination of the transport properties of the redox couple from steady-state voltammetry. The apparent diffusion coefficient (D_{app}) of I^- and I_3^- was calculated from the limiting currents (I_{lim}) of the steady-state voltammetry, corresponding to the reactions $I_3^- \quad 3I^- + 2e^-$, using the following equation:

$$I_{lim} = 4nFD_{app}rc \tag{1}$$

where n is the number of transferred electrons, F is the Faraday constant, r is the microdisk electrode radius, and c is the bulk concentration of the electroactive species. The apparent diffusion coefficient was assumed to be an average of the diffusion coefficients of I^- and I_3^-. The physical diffusion coefficient could be obtained from the anodic and cathodic limiting currents. However, it is impossible to separate D_{ex} between I^- and I_3^- from D_{phys} of I^- and I_3^-, when the exchange-reaction-based diffusion process is predominant. D_{app} can be obtained from the Dahms–Ruff equation,[11]

$$D_{app} = D_{ex} + D_{phys} = {}^1\!/\!_6 k_{ex}\delta^2 c + D_{phys} \tag{2}$$

where k_{ex} is the exchange-reaction rate constant and δ is the center-to-center inter-site distance at the exchange reaction. D_{app} increases linearly with increasing concentration of the redox couple when D_{ex} and D_{phys} are conjugated. If the exchange reaction does not occur or contributes only minimally to the total charge transport process, the following equation can hold:

$$D_{app} = D_{phys} \tag{3}$$

D_{app} does not change with concentration, so long as the viscosity does not change.

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*mwatanab@ynu.ac.jp

The dependence of the apparent diffusion coefficient of the redox couple in EMImTFSI and PEGDE on the concentration is shown in Fig. 1. When the ionic liquid is used as an electrolyte, D_{app} proportionally increases with increasing concentration. In the case of $[I^-] : [I_2] = 1.5 : 1$ in EMImTFSI, the change in D_{app} depending on the concentration of the redox couple is larger than the change observed in other systems. In contrast, D_{app} is constant or slightly decreases on increasing the concentration of the redox couple in PEGDE, because the viscosity increases with increasing concentration. D_{phys} of the systems $[I^-] : [I_2] = 1.5 : 1$ (in EMImTFSI), $[I^-]: [I_2] = 4 : 1$ (in EMImTFSI), $[I^-] : [I_2] = 1.5 : 1$ (in PEGDE), $[I^-] : [I_2] = 4 : 1$ (in PEGDE) calculated from the intercepts are $1 \times 10^{-7}, 2 \times 10^{-7}, 2 \times 10^{-7}$, and $1 \times 10^{-7}\,cm^2\,s^{-1}$, respectively. D_{phys} approximately depended on the viscosities. Exchange-reaction-based diffusion occurs not only in EMImTFSI but also in various ionic liquids.

It is considered that the exchange reaction occurs by the following process:

$$I^- + I_3^- \rightarrow I^-\cdots I_2\cdots I^- \rightarrow I_3^- + I^-$$

When I_2 is exchanged from I_3^- to I^-, I^- and I_3^- should be in close proximity with each other. The collision between I^- and I_3^- is generally difficult, since both of the reactants are negatively charged. The ionic liquids consist only of ions, and the molar concentration is very high. The molar concentration of EMImTFSI itself is 3.88 M at 25 °C.[12] Therefore, the redox couple in the ionic liquids exists in a strong ionic strength field. The two negatively changed ions (I^- and I_3^-) can collide with each other more easily in the ionic liquids than in the molecular liquids by "the kinetic salt effect".[13] This consideration is also supported by an old observation[11c] that exchange-reaction-based diffusion of an I^-/I_3^- redox couple was obvious in high ionic strength (5 M) aqueous solutions. It may not be ruled out that the exchange reaction in PEGDE is disturbed by factors other than the ionic strength effect. However, the exchange-reaction-based diffusion could not also be observed in acetonitrile even at high redox couple concentrations.

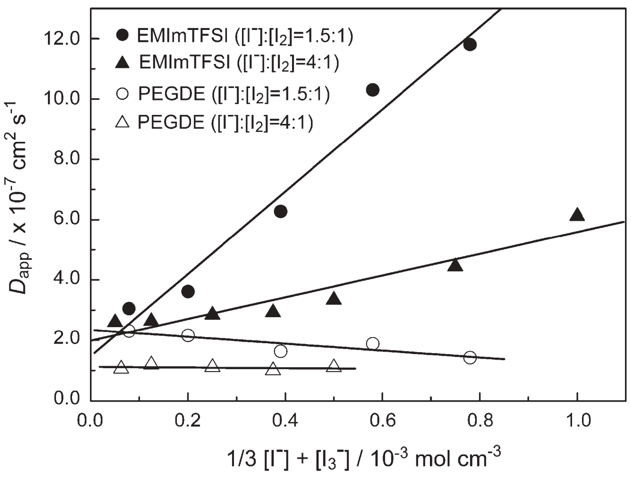

Fig. 1 Relationship between D_{app} and the concentration of the I^-/I_3^- redox couple with different molar ratios dissolved in EMImTFSI and PEGDE.

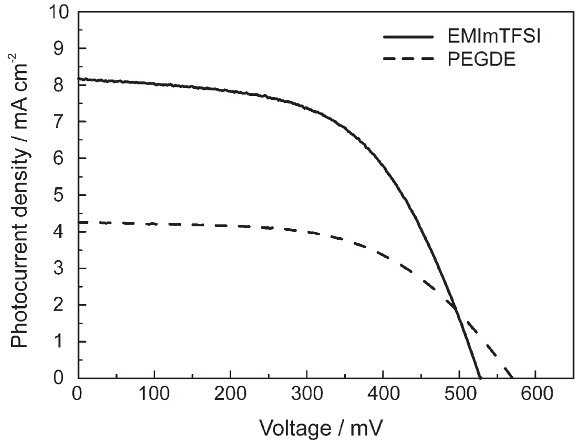

Fig. 2 Photocurrent density *vs.* photovoltage curves obtained for DSSCs with EMImTFSI and PEGDE. Each electrolyte contains the I^-/I_3^- redox couple ($[I^-] + [I_3^-] = 1.0$ M, $[I^-] : [I_2] = 4 : 1$) in each solvent (active area = 0.45 cm^{-2}).

Fig. 2 presents the photocurrent density *versus* voltage curves for DSSCs with EMImTFSI and PEGDE electrolytes under the irradiation of AM1.5 sunlight. The DCCSs were prepared according to the same procedure as described in ref. 9. The short-circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF) of the DSSC with EMImTFSI are 8.2 mA cm^{-2}, 528 mV, and 0.56, respectively, yielding an overall energy conversion efficiency (η) of 2.4%. For the DSSC with PEGDE, the corresponding device parameters (J_{sc}, V_{oc}, FF, and η) are 4.3 mA cm^{-2}, 570 mV, 0.56, and 1.4%, respectively. The J_{sc} of the cell with PEGDE is a reasonable value, if it is compared with the calculated value of 5.6 mA cm^{-2} that can be obtained by referring to a comprehensive analysis of the diffusion and migration processes in the steady-state operation of DSSCs.[14]

The value of J_{sc} using the molecular solvent is about 50% of that using the ionic liquid, although both solvents dissolved the same concentration and molar ratio of the redox couple and have similar viscosities. The difference in conversion efficiency is smaller than that in J_{sc}, because the open-circuit voltage (V_{oc}) using EMImTFSI is lower than that using PEGDE. We reported previously that 1-ethyl-3-methylimidazolium dicyanamide (EMImDCA) with the same solutes demonstrated high performance as the electrolyte.[9] The difference in the conversion efficiencies of the DSSCs using PEGDE and EMImDCA as the electrolytes is more than doubled. From these results, it is revealed that the fast charge transport, occurring in the ionic liquids, is effective for the DSSCs.

In conclusion, the charge transport of an I^-/I_3^- redox couple in EMImTFSI (ionic liquid) and in PEGDE (molecular liquid) was found to be completely different. The characteristic charge transport based on the exchange reaction of the I^-/I_3^- redox couple was revealed to occur only in the ionic liquid, although the physical diffusion of the redox couple in EMImTFSI and PEGDE was similar. DSSCs using EMImTFSI and PEGDE as the electrolytes were prepared, and the cell performances were presented. The photocurrent density of the cell using the ionic liquid was twice as high as that using the molecular solvent.

So far, the main advantages of the ionic liquids for electrochemical devices have been considered to be non-volatility and non-flammability. However, it is revealed for the first time that the high ionic strength of ionic liquids can be significant advantages, when they are applied to the DSSCs.

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Ryuji Kawano and Masayoshi Watanabe*
Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan.
E-mail: mwatanab@ynu.ac.jp; Fax: +81-45-339-3955;
Tel: +81-45-339-3955

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