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Equilibrium potentials and charge transport of an I^-/I_3^- redox couple in an ionic liquid

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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Equilibrium potentials and charge transport of an I^-/I_3^- redox couple in an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, are revealed by using a microelectrode technique, where the anomaly of the charge transport at high concentrations of the redox couple with comparable $[I^-]$ and $[I_3^-]$ can be attributed to the exchange reaction of $I^- + I_3^- \rightarrow I_3^- + I^-$.

Dye-sensitized nanocrystalline solar cells present an important alternative to current solar cell technology.[1] The solar cell is constituted by nanocrystalline TiO_2, a molecular dye and an electrolyte containing a redox couple.[2] The function of such devices is based on the injection of an electron from a photoexcited state of the sensitizer dye into a conduction band of the nanocrystalline semiconductor.[3] These cells employ a liquid electrolyte to reduce the dye cation, generated by the injection of the photoexcited electron. Typically, an iodide/triiodide (I^-/I_3^-) redox couple dissolved in acetonitrile is used.[3] However, when such volatile solvents are used, the cell is deteriorated by evaporation of the solvent over extended use. Ionic liquids[4] have unique properties such as non-volatility,[5] non-flammability,[5] high ionic conductivity[6] and gel-forming properties with polymers,[7] and have been applied to solar cells.[5] However, the fundamental properties of the I^-/I_3^- redox couple in ionic liquids, including the equilibrium potentials and the charge transport mechanism, have not been revealed yet, although these properties are crucial for the performance of the solar cells in terms of the open-circuit potential and the short-circuit current. Furthermore, there has been reported an anomaly of solar cell performance when ionic liquids are used as electrolytes, such as high short-circuit current in spite of high viscosities.[5] In this study, the fundamental properties have been elucidated using a microelectrode technique, especially focusing on the anomaly of the charge transport.

The ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMImTFSI), was used,[4] and 1-ethyl-3-methylimidazolium iodide (EMImI) and I_2 were dissolved in it as a redox couple. A microelectrode technique was employed for the electrochemical measurements[8] in order to simplify determination of the equilibrium potential and transport property of the redox couple from steady-state voltammetry. A Pt microdisk electrode (12 μm diameter) was used as the working electrode, while a Pt (0.3 mm diameter) disk electrode was used as the counter electrode. An iodine reference electrode, consisting of a Pt wire immersed in an EMImTFSI solution containing EMImI and I_2 ($[\mathrm{EMImI}]:[I_2] = 4:1$ and $[I^-] + [I_3^-] = 1$ M) was employed in this study ($E = -0.21$ V *vs.* ferrocene/ferrocenium internal standard). It was assumed that I^- and I_2 immediately formed I_3^- when they were mixed. All the samples were prepared in an Ar-filled glove box, and the electrochemical measurements were conducted under Ar atmosphere at 25 °C.

Microelectrode cyclic voltammograms for the I^-/I_3^- redox couple mixtures are shown in Fig. 1. Two-step sigmoidal responses were observed for both of the mixtures. For the EMImI and I_2 equimolar mixture (Fig. 1a), the cathodic current corresponds to the reduction of I_3^-, and the anodic current corresponds to the oxidation of I_3^-. As the molar ratio between EMImI and I_2 is changed to 4:1 (Fig. 1b), the oxidation of I^- to I_3^- is additionally observed. This oxidation current was also observed in all mixtures of $[\mathrm{EMImI}]/[I_2] > 1$. When one critically compares the two voltammograms, the magnitude of current does not reflect the concentration of each redox species. However, this kind of anomaly was reproducibly observed in this system. From these cyclic voltammograms, the equilibrium potentials of EMImI/I_2 mixtures in the ionic liquid can be clearly determined as the potentials where the voltammetric currents become zero. In the conventional dye-sensitized solar cells, the oxidation reaction ($3I^- \rightarrow I_3^- + 2e^-$) is considered to occur at the dye-sensitized TiO_2 anode, while the reduction reaction ($I_3^- + 2e^- \rightarrow 3I^-$) is considered to occur at the counter cathode. To ascertain the voltammetric assignment of this reaction, the number of transferred electrons (n) was calculated from the Nernst equation using the equilibrium potentials of the voltammograms and the concentration of the redox-active species. In every composition, n was found to be 2. This verifies the assignment of the reaction in the ionic liquid mixtures. The equilibrium potentials of the ionic liquid mixtures, ranging from −15 mV to 159 mV, increased with decreasing the concentrations ($[I^-] + [I_3^-]$) and with decreasing $[\mathrm{EMImI}]/[I_2]$ ratios. The open-circuit voltages of our preliminarily constructed solar cells changed in a similar manner to the equilibrium potentials of the redox couple in the ionic liquid.

The diffusion-limited currents, corresponding to the reaction ($I_3^- + 2e^- \rightleftharpoons 3I^-$), are given by

$$I_{\mathrm{lim}} = 4Fr\{(2/3)D_{I^-}[I^-] + 2D_{I_3^-}[I_3^-]\} \quad (1)$$

where F is the Faraday constant, r is the microdisk electrode radius, and D_{I^-} and $D_{I_3^-}$ are diffusion coefficients of I^- and I_3^-, respectively. Here, we assume $D_{I^-} = D_{I_3^-} = D$, since exchange-reaction-based diffuison (*vide infra*) does not discriminate D_{I^-} and $D_{I_3^-}$ and is affected by the total concentration of the redox species ($1/3[I^-] + [I_3^-] = c$). Eqn. (1) can be rewritten as

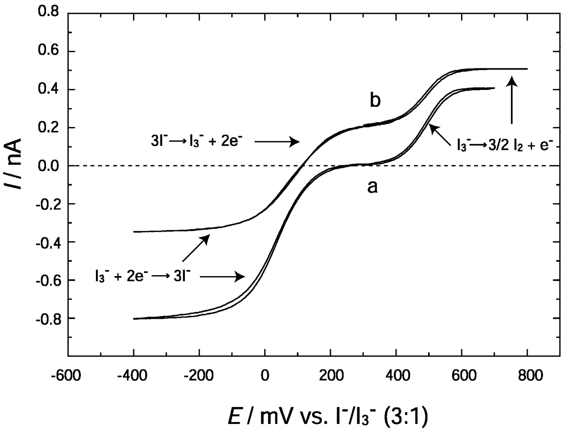

Fig. 1 Cyclic voltammograms (scan rate, $v = 2$ mV s^{-1}) at a Pt disk (12 μm in diameter) electrode using an iodine reference electrode: $[I^-] + [I_3^-] = 10$ mM; (a) $[\mathrm{EMImI}]/[I_2] = 1/1$ ($[I^-]/[I_3^-] = 0/1$); (b) $[\mathrm{EMImI}]/[I_2] = 4/1$ ($[I^-]/[I_3^-] = 3/1$).

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$$I_{\mathrm{lim}} = 8FDrc \qquad (2)$$

Fig. 2 shows the limiting currents as a function of c. Eqn. (2) predicts that the limiting current linearly increases with the concentration, if D is not dependent on the concentration. This is the case for [EMImI]:[I_2] = 10:0, 10:1, and 1:1. Significantly, the limiting currents of the I^-/I_3^- ionic liquids with the other compositions increase nonlinearly. Such an anomaly is possible if the viscosities of the I^-/I_3 ionic liquids nonlinearly decrease with the concentration. However, the viscosities at 25 °C of the ionic liquids containing I^-/I_3^- redox couple ranged from 25.8–34.0 mPa s, depending on the redox couple concentrations, and the change was not so large as is seen in the limiting currents (Fig. 2). Thus, the nonlinear increase should be attributed to another mechanism. When simple physical diffusion and exchange reaction are conjugated, D can be obtained from the Dahms–Ruff equation;[9]

$$D = D_{\mathrm{phys}} + 1/6k_{\mathrm{ex}}\delta^2c \qquad (3)$$

where D_{phys} is the physical diffusion coefficient, k_{ex} is the exchange-reaction rate constant, and δ is the center-to-center intersite distance at the exchange reaction. The exchange reaction here can be expressed by

$$I^- + I_3^- \xrightarrow{k_{\mathrm{ex}}} I_3^- + I^-$$

The second term in eqn. (3), *i.e.*, $1/6k_{\mathrm{ex}}\delta^2c$, is the exchange-reaction-based diffusion coefficient (D_{ex}). Substituting eqn. (3) in eqn. (2), the following equation can be derived.

$$I_{\mathrm{lim}} = 8Frc(D_{\mathrm{phys}} + D_{\mathrm{ex}}) = 8Fr(D_{\mathrm{phys}}c + 1/6k_{\mathrm{ex}}\delta^2c^2) \qquad (4)$$

Consequently, when only a physical diffusion process occurs, the limiting current should follow the first-order increase with increasing concentration. In the case of the conjugation of physical diffusion and exchange reaction processes in ionic liquids, the limiting current is proportional to the second-order of concentration. Thus, the linear increases ([EMImI]:[I_2] = 10:0, 10:1, and 1:1) were analyzed by fitting the results using eqn. (4) with an assumption of $1/6k_{\mathrm{ex}}\delta^2c = 0$, and the second-order increases were analyzed using eqn. (4). The D_{phys} and D_{ex} were estimated so as to maximize the correlation coefficients (R^2). The results are summarized in Table 1. The fitting was excellent as can be seen from $R^2 > 0.98$. The solid lines in Fig. 2 were drawn from the obtained fitting parameters and eqn. (4). Since D_{ex} contains a concentration term, the magnitude of D_{ex} was calculated at two different concentrations (Table 1). The physical diffusion, D_{phys}, resulting from the ionic diffusion process of I^- and I_3^- is of the order of 10^{-7} cm² s^{-1} from these electrochemical measurements. This value is in good agreement with the self-diffusion coefficients of $EMIm^+$ and $TFSI^-$ in the EMImTFSI bulk obtained from the pulsed-gradient spin-echo NMR measurements.[10] The exchange-reaction-based diffusion coefficient, D_{ex}, is found to be *ca*. 10^{-9} cm² s^{-1}, which is a minor contribution compared with the physical diffusion, when the concentration is low (0.01 M). However, at a high concentration (1.0 M), the D_{ex} values are larger than those of the physical diffusion. The D_{ex} becomes larger when the molar ratio of [EMImI] and [I_2] is comparable, although it is negligible at [EMImI]/[I_2] = 1. As the result, when concentration of the redox species is high, and [I^-] and [I_3^-] are comparable, the contribution from the exchange reaction dominates the charge transport in this system. At present, it is not clear whether the exchange reaction is accompanied by an electron exchange reaction or is a simple exchange reaction of I_2 between I^- and I_3^-.

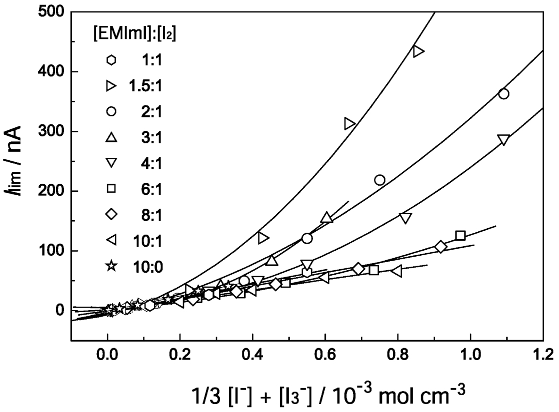

Fig. 2 Limiting currents for the reaction of $I_3^- + 2e^- \rightleftharpoons 3I^-$ as a function of concentration (1/3 [I^-] + [I_3^-]) for EMImI/I_2 redox couple with different molar ratios dissolved in EMImTFSI.

Table 1 Physical diffusion (D_{phys}) and exchange-reaction-based diffusion (D_{ex}) coefficients of EMImI/I_2 in EMImTFSI.

		$D_{\mathrm{ex}}/10^{-7}$ cm² s^{-1}		
I^-:I_2	$D_{\mathrm{phys}}/$ 10^{-7} cm² s^{-1}	0.01 M[a]	1.0 M[a]	R^2
1:1	2.74	—	—	0.997
1.5:1	2.83	0.094	9.40	0.981
2:1	2.63	0.035	3.54	0.988
3:1	0.49	0.053	5.34	0.995
4:1	0.93	0.025	2.53	0.996
6:1	1.28	0.008	0.76	0.997
8:1	1.72	0.005	0.48	0.999
10:1	1.98	—	—	0.992
10:0	2.68	—	—	0.997
$EMIm^+$	6.35[10]	—	—	—
$TFSI^-$	3.54[10]	—	—	—

[a] [I^-] + [I_3^-].

In conclusion, the microelectrode technique has enabled us to determine the equilibrium potentials and the charge transport rate of an I^-/I_3^- redox couple in an ionic liquid. The anomaly of the charge transport is revealed to be caused by the contribution of the exchange reaction between I^- and I_3^-, which is the major contribution to the total charge transport process when concentration of the redox couple is high, and [I^-] and [I_3^-] are comparable.

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