Equilibrium Potential and Charge Transport of an I^- / I_3^- Redox Couple in an Ionic Liquid

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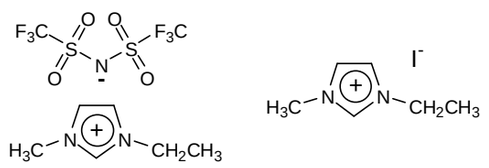
Dye-sensitized nano-crystalline solar cells present an important alternative to current solar technology. Photo-electrochemical cells based on sensitization of nano-crystalline TiO_2 by molecular dyes have attracted great attention since their first announcement as efficient photovoltaic devices.[1] The function of such devices is based on the injection of an electron from a photo-excited state of the sensitizer dye into the conduction band of the nano-crystalline semiconductor. These cells typically employ a liquid electrolyte to reduce the dye cation. Usually an iodide/tri-iodide redox (I^-/I_3^-) active couple dissolved in acetonitrile is used for this purpose. However, when such volatile solvents are used, the cell is deteriorated by evaporation of solvent in a long time use. Ionic liquids have unique properties such as non-volatility, non-flammability, relatively high conductivity[2] and gel-forming property with polymers,[3] and have been applied to the solar cells.[4] However, fundamental properties of an (I^-/I_3^-) redox couple in ionic liquids, including the equilibrium potentials and the charge transport mechanism, have not been revealed yet. In this study, the fundamental properties have been elucidated by using microelectrode technique and the advantages and disadvantages of the redox active ionic liquids as the charge transport layer of the solar cells will be discussed.

As the ionic liquid, 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide (EMImTFSI) was used, and EMImI and I_2 were dissolved in it as a redox couple (Fig. 1). Fig. 2 shows steady-state microelectrode voltammograms of EMImI / I_2 mixtures. Since the redox responses are dependent on the [EMImI] / [I_2] ratios, the reactions occurring in the ionic liquid can be assigned, as shown in the figure.

The equilibrium potentials of EMImI / I_2 mixtures in the ionic liquids can be clearly determined from the potentials where the currents become zero. The equilibrium potentials increased with decreasing the [EMImI] / [I_2] ratios and with decreasing the concentrations ([EMImI] + [I_2]).

Limiting currents (I_{lim}) in these measurements, corresponding to the reaction ($I_3^- + 2e^- \blacksquare 3I^-$) which is believed to occur in the solar cells, are given by $I_{lim} = 4nFCDr$. D is average diffusion coefficient of I^- and I_3^- and seems to includes both physical diffusion and electron hopping in such viscous media. When diffusion coefficient includes physical diffusion and electron hopping,[5] D is expressed by $D = D_{phys} + 1/6k_{ex}\delta^2C$, where k_{ex} the electron self-exchange rate constant, δ the center-to-center interstice distance at electron transfer. The limiting currents were measured by changing both EMImI concentration and the [EMImI] / [I_2] ratios, as shown in Fig. 3. Non-linearity of the plots in Fig. 3 allows us to separate the physical diffusion and the electron hopping based on the electron exchange reaction between I^- and I_3^-. The contribution of the electron hopping becomes predominant when the concentration is high, and [I^-] and [I_3^-] are comparable.



EMImTFSI EMImI

Fig. 1 Structure of ionic liquid and iodine redox.

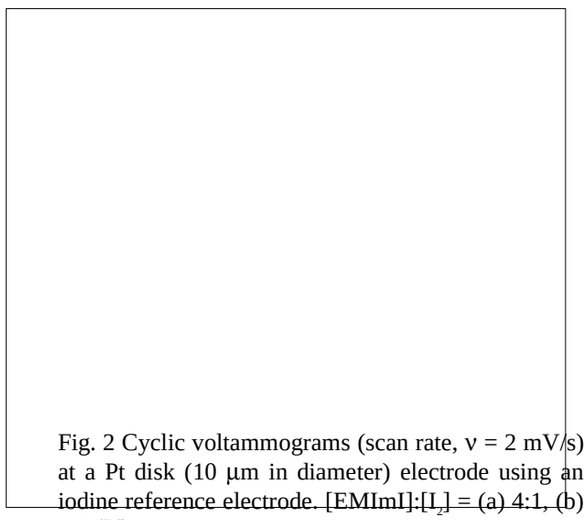


Fig. 2 Cyclic voltammograms (scan rate, ν = 2 mV/s) at a Pt disk (10 μm in diameter) electrode using an iodine reference electrode. [EMImI]:[I_2] = (a) 4:1, (b) 1:1 (I_3^-)

Fig. 3 Limiting currents vs. concentration plots for cyclic voltammetric measurements of I^- and I_2 with different molar ratios and with different concentrations.

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