

Performance of Dye-sensitized Solar Cells using Ionic Liquids as their Electrolytes

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INTRODUCTION

Recently, there has been a considerable interest on the innovation of cost-effective solar cells. The dye-sensitized solar cells (DSSCs) have been the subject of intense study for their low cost and reasonably high efficiency, compared to the conventional Si and GaAs cell. The DSSCs are constituted by highly porous nano-crystalline TiO₂, monolayer of dye molecules adsorbed on the TiO₂, and electrolytes containing a redox couple. The electrolytes employ highly volatile and flammable organic solvents, which significantly reduce their long-term stability and safety. We have reported the use of ionic liquids as electrolytes for DSSCs as replacements of organic solvents.¹⁾ The Ionic liquids are room temperature molten salts and consist of only cations and anions. Because of their unique chemical and physical properties, such as high conductivity, wide electrochemical window, non-volatility, thermal stability, and non-flammability, the ionic liquids seem to be the most appropriate solvents to solve such problems.

In spite of the high viscosity compared to organic solvents, high short-circuit current is revealed in DSSCs using ionic liquids. This is explained by a conduction mechanism in polyiodides chain via a Grotthuss or a relay mechanism. Recently, we succeeded to separate the contributions of physical diffusion and exchange-reaction-based diffusion of an I/I₃⁻ redox couple to the electron transporting processes in various ionic liquids.²⁾ However, the V_{oc} of the cells with ionic liquids are still lower than those of the cells using organic solvents, which restricts the use of ionic liquids for DSSCs. The properties of ionic liquids can be tuned by controlling the structures of the cations and anions. Thus far, most of the studies have been concerned with ionic liquids with iodide anions for the advantage of the high concentration of I⁻. However, the viscosity of such ionic liquids is comparatively high. In this study, we prepared ionic liquids having different physicochemical properties by the combination of different cations and anions (Fig. 1) and investigated their effect on the performances of DSSCs to find the most suitable ones as the electrolyte of DSSCs. EMImI and I₂ were used as a redox couple dissolved in each ionic liquids at various concentrations. In other words, the ionic liquids were used as a solvent, which offered the ionic liquids various characteristics, for example, lower viscosity than those of the ionic liquids having iodide counter anion.

EXPERIMENTAL

A ultra-microelectrode technique was employed for cyclic voltammetry (CV) measurements. A Pt microdisk electrode (10 μm diameter) was used as the working electrode and a Pt disk electrode (1.0 mm diameter) was used as the counter electrode, while a Pt wire immersed in each ionic liquids containing EMImI and I₂ ([EMImI]:[I₂]

= 4:1, total concentration is 1.0 M) was employed as an iodine reference electrode. All the samples were prepared in a N₂ atmosphere glove box, and the CV measurements were conducted under N₂ atmosphere at room temperature.

$I-V$ measurements were performed in air using an open sandwich type cell. The nanostructured working electrode was prepared from colloidal TiO₂ (Solaronix Ti-Nanoxide T) deposited on a transparent, conducting glass sheet. N3 was used as a dye. Active area of the cells was typically 0.45 cm². AM 1.5 solar simulator (100 mW cm⁻²

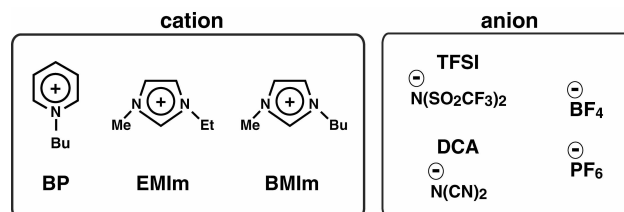


Fig. 1 Molecular structures of ionic liquids.

²⁾ was used for all of the measurements.

RESULTS AND DISCUSSIONS

The DSSCs performances were significantly influenced by difference in the properties of the ionic liquids. The equilibrium potential of the redox couple (EMImI:I₂ = 10:1) dissolved in various ionic liquids at different concentrations were obtained from the CV measurements. The V_{oc} 's were acquired from $I-V$ measurements of DSSCs, and both the equilibrium potential and the V_{oc} are plotted in the same scale. The equilibrium potentials were adjusted against Fc/Fc⁺ in each ionic liquids in order to make a realistic comparison. An analogous change was found in the equilibrium potential and the V_{oc} with different concentrations and type of ionic liquids. However, the ionic liquids, which are comprised of a DCA anion, exhibit a considerably larger V_{oc} value than predicted from their equilibrium potentials. Using DCA as an anion of DSSCs electrolyte, solar cell performances were almost independent of the cation structure, and this indicates that the V_{oc} of the DSSCs could be explained in terms of the properties of the anion. Thus, we focus attention on the donicity of the anion, and measured it by using a solvachromic Lewis-base indicator. It is known that the donicity of ionic liquids depend on the anion rather than cation. Our results show that ionic liquids with DCA anion have substantially higher donicity than that of TFSI, BF₄ and PF₆ ionic liquids, which compared well with the equilibrium potential. 4-*t*-Butylpyridine (TBP) is often used as a basic additive to improve the V_{oc} , and the presence of DCA anion in a solar cell system might have a similar effect on gaining higher V_{oc} values. The photo-energy conversion efficiency of DSSCs with BPDCA containing only a redox couple (EMImI and I₂) can be optimized up to 5.5%. Therefore, the use of ionic liquids, which have an anion of high donicity is preferable for obtaining a high V_{oc} that leads to the superior performance of DSSCs.

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