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Electrochemical characterization and photovoltaic performance of the binary ionic liquid electrolyte of 1-methyl-3-propylimidazolium iodide and 1-ethyl-3-methylimidazolium tetrafluoroborate for dye-sensitized solar cells

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ABSTRACT

Determination of triiodide diffusion coefficient, charge-transfer resistance and photovoltaic performance of the binary ionic liquid electrolyte of 1-methyl-3-propylimidazolium iodide (MPII) and 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) for dye-sensitized solar cells (DSSCs) were performed at varying volume ratios of MPII/$EMIMBF_4$. Compared to pure MPII ionic liquid, the addition of $EMIMBF_4$ not only increased triiodide diffusion coefficient, but also decreased charge-transfer resistance at Pt/electrolyte interface, leading to the notably improved photovoltaic performance of DSSC. The highest photoelectric conversion efficiency of 4.99% was obtained under light intensity of 100 mW/cm^2 for the DSSC with the binary MPII/$EMIMBF_4$ ionic liquid electrolyte when the volume ratio of MPII/$EMIMBF_4$ was 50/50, which was much higher than that of pure MPII ionic liquid electrolyte (2.6%).

1. Introduction

Dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO_2 semiconductors have attracted much attention because of their low-cost production and high photovoltaic performance [1,2]. Although an impressive 11% light-to-electricity conversion efficiency has been achieved for DSSCs with organic solvent-based electrolytes [3], the presence of volatile liquid electrolyte in such devices results in some practical limitations for sealing and long-term operation of the devices. A good alternative to organic solvents, e.g. for electrochemical devices, are ionic liquids [4,5], due to their attractive chemical and thermal stability, non-volatility, and high ionic conductivity at room temperature [6]. Among the ionic liquid electrolytes used in DSSCs, most attention has been paid to the ionic liquids with 1,3-dialkylimidazolium cations [7], especially to 1-methyl-3-propylimidazolium iodide (MPII), an iodide source in the electrolyte. However, the energy conversion efficiency of DSSCs using ionic liquid solvents could not reach that of DSSCs with volatile liquid solvent due to the high viscosity of MPII (880 mPa at 21 °C) [8,9]. It has been reported that mixing some imidazolium melts containing nonelectroactive anions with MPII could decrease the viscosity of the electrolyte and improved the power conversion efficiencies of DSSCs [10–12]. The conversion efficiency of DSSC based on amphiphilic ruthenium sensitizer Z907 [11] was improved from 6% to 7% by the addition of 1-methyl-3-ethylimidazolium dicyanamides (EMIDCN) into MPII electrolyte. A stable DSSC also using sensitizer Z907 with a high conversion efficiency of 6.4% has been reported under simulated full sunlight (Air Mass 1.5, 100 mW/cm^2) using a binary ionic liquid electrolyte of MPII and 1-ethyl-3-methylimidazolium thiocyanate (EMINCS) [12].

In this study, imidazolium melts 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) was used to improve conversion efficiency of DSSC due to its low viscosity (37 mPa at 25 °C [13]), high ionic conductivity [14], high electrochemical stability [15], and environment friendly. Although Zistler et al. [16] have recently reported the temperature dependent impedance analysis of binary ionic liquid electrolytes including $EMIMBF_4$/MPII, the study about the effect of the binary ionic electrolytes $EMIMBF_4$/MPII on the performance of solar cells has not reported yet. In this paper, the electrolytes with various volume ratios of MPII/$EMIMBF_4$ were analyzed via polarization measurements and electrochemical impedance spectroscopy (EIS). The effect of volume ratio of MPII/$EMIMBF_4$ on the photovoltaic performance of DSSC was studied. The highest conversion efficiency of 4.99% was achieved when

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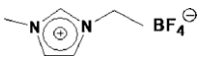

Scheme 1. Molecular structure of $EMIMBF_4$ ionic liquid.

the volume ratio of MPII/$EMIMBF_4$ was 50/50, which was much higher than that of pure MPII ionic liquid electrolyte.

2. Experimental

2.1. Materials

The dye cis-$(SCN)_2$bis(2,2′-bipyridyl-4,4′-dicarboxylate) ruthenium (N3) was purchased from Solaronix SA. Titanium(IV) isopropoxide, 4-tert-butylpyridine (TBP) and 1-methyl-3-propylimidazolium iodide (MPII) were purchased from Aldrich. All the materials were reagent grade and used as received. The synthesis of ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$) was carried out according to methods reported by Matsumoto et al. [17], and its molecular structure is shown in Scheme 1.

2.2. Sample preparation

Symmetric Pt electrochemical thin-layer cells were prepared for polarization curve and impedance spectroscopy measurements [18,19]. The cell consisted of two identical platinized, TCO-coated glass substrates (FTO, 20 Ω/square) sealed with a surlyn film (30 μm, DuPont). The cell was filled with the ionic liquid electrolyte at varying volume ratio of MPII/$EMIMBF_4$. All the measurements were performed at room temperature.

The TiO_2 (anatase) colloidal paste was prepared by hydrolysis of titanium tetraisopropoxide according to the previously reported process [20]. The TiO_2 paste was deposited using a simple doctor blade technique on completely cleaned FTO glass (4 mm thick, 75% transmittance in the visible, 20 Ω/square). The thickness and the size of the porous TiO_2 layer were controlled by an adhesive tape. Afterward, the film was heated at 450 °C for 60 min. The thickness of the resulting porous TiO_2 film was about 8 μm. Coloration of TiO_2 was carried out by soaking the film in dry ethanol containing 2.5×10^{-4} M N3 ruthenium complex for 20 h at room temperature. In order to avoid rehydration of the TiO_2 surface or capillary condensation of water vapor from ambient air inside the nanopores of the film, the dye adsorption was done immediately while the electrode was still hot, *i.e.*, its temperature was *ca.* 80 °C. A sandwich cell was prepared with a second conducting glass coated with Pt film, which was deposited from paste containing hexachloroplatinic acid, ethylcellulose and terpineol by screen printing process. The two electrodes were separated by a 30 μm surlyn spacer and sealed up by heating at 150 °C. The redox electrolyte was introduced into the space of inter-electrodes through the two holes predrilled on the back of the counter electrode. The two holes were sealed up using a surlyn film, on which a glass slide was pressed under heat. The redox electrolyte composed of 0.15 M I_2, 0.5 M 4-tert-butylpyridine and 0.1 M guanidinium thiocyanate in a mixture of MPII and $EMIMBF_4$ (the volume ratio of MPII/$EMIMBF_4$ ranging from 100% to 20%). The active area of DSSC was 0.194 cm^2.

2.3. Measurement

Viscosity measurements were conducted using a 4ARES-9a rheometer (Rheometric Scientific, USA) at room temperature. The viscosities given were averaged over the values obtained at shear rates from 10 to 1000 s^{-1}. Polarization curves and impedance spectroscopy measurements were performed using an IM6/IM6e (Zahner, Germany) electrochemical analyzer in a two-electrode configuration. A 10 mV AC perturbation was applied and the frequency range was 0.01–100 kHz. The scan rate was 10 mV/s. Photocurrent–voltage curves were recorded using a source meter (Keithley-2400, Keithley Co. Ltd., USA) under an illumination of 100 mW/cm^2 (1.5G Air Mass Filter, 1sun) from a 300 W Oriel solar simulator 91,160 at room temperature. The output beam size of the solar simulator was 2 × 2 in. The size of the cells was about 1 cm^2. A mask of 0.194 cm^2 was clipped on the TiO_2 side to define the active area of the cell.

3. Results and discussion

Generally, a DSSC comprises a dye-sensitized nanocrystalline porous TiO_2 film immobilized on a transparent conducting oxide TCO-coated glass substrate, an electrolyte containing an I^-/I_3^- redox couple, and a platinized TCO-coated glass substrate as counter electrode. When the sensitizer dye molecules absorb solar energy, electrons are injected rapidly from the excited state of the dye into the conduction band of TiO_2. The injected electrons diffuse into the conduction band of TiO_2 and reach the outer circuit through the back contact. The oxidized dye molecules are reduced by I^- ions in the electrolyte via the reaction $3I^- \rightarrow I_3^- + 2e$, where

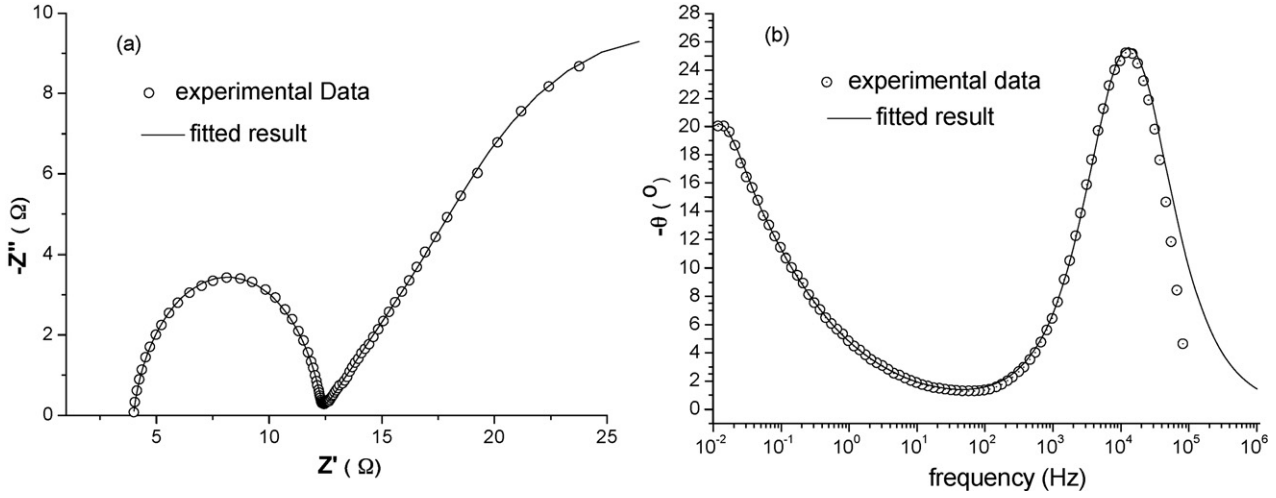

Fig. 1. (a) Typical Nyquist plot and (b) Bode plot of the impedance spectrum of the binary ionic liquid electrolyte (MPII/$EMIMBF_4$ volume ratio 20/80) measured at a thin layer cell.