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Dye-sensitized solar cells using ion-gel electrolytes for long-term stability☆

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ABSTRACT

Dye-sensitized solar cells (DSSCs) with quasi-solid ion-gel electrolytes are fabricated using a 1-propyl-3-methyl imidazolium iodide (PMII) with a small amount of poly(styrene-block-ethyleneoxide-block-styrene) (SEOS) triblock copolymer. The interaction between the PMII and SEOS changes the liquid state of PMII into a solid state, and the interactions between the imidazolium cation of PMII and the ethyleneoxide of SEOS are confirmed by an ab initio method. The phase change of the electrolyte from an ionic liquid to a quasi-solid ion-gel in a DSSC slightly increases the photoconversion efficiency, and the DSSC containing an ion-gel maintains 92% of its efficiency under more than 1440 h of operation, which is higher than that with the ionic liquid as an electrolyte (78%) in this system. The addition of dendrons as a barrier-forming co-adsorbent increases the short-circuit current density (J_{sc}) of the DSSC. Up to a 27% increase in the power conversion efficiency are achieved with the G5 dendron as the co-adsorbent. EIS and IPCE measurements show that the increase in J_{sc} is due to the suppression of recombination by the surface coverage of the TiO_2 particles. The photocurrent and the conversion efficiency for all DSSCs prepared with quasi-solid ion-gel electrolytes and dendron co-adsorbents are higher than those prepared with an ionic liquid.

1. Introduction

Dye-sensitized solar cells (DSSCs) have received tremendous attention as the next generation of solar cells due to their low production costs and reasonable energy conversion efficiency of more than 11% [1,2]. The principle of energy conversion in DSSCs is based on the injection of electrons from a photoexcited state of a dye that is attached to a mesoporous TiO_2 semiconductor into the conduction band of the semiconductor. The oxidized dyes can be reduced by a redox mediator (for example, I^-/I_3^-) present in the electrolyte located between two electrodes, which must also be re-reduced at the counter-electrode, making the photoelectrochemical cell regenerative. Because the common matrix for the redox mediator is a liquid organic solvent such as volatile acetonitrile, the packaging of liquid-electrolyte DSSCs requires perfect sealing to avoid leakage, evaporation of the solvent and contamination by impurities for practical usage [3].

Several attempts have been made to substitute liquid electrolytes with room-temperature ionic liquids (RTILs), which have negligible vapor pressure [4], but the leakage problem has not been overcome. Therefore, solid- or quasi-solid state electrolytes such as solid polymer electrolytes [5–10], polymer gel electrolytes [11–13], and organic hole-transport materials [3,14] have been studied to address the drawbacks of liquid electrolytes. However, the increased viscosity of the medium leads to low and limited redox mediator transport [15] and/or an insufficient penetration of the electrolyte into the nanoporous TiO_2 photoelectrode [16], which in turn leads to lower photovoltaic performance when compared to DSSCs assembled with liquid electrolytes [17]. From this point of view, we have focused on an ion-gel electrolyte based on RTILs possessing high ionic conductivity to minimize leakage and maintain the feasibility of liquid-phase redox mediator transport.

It is reported that some RTILs become gels with the addition of polymers [18] and provide reasonably strong mechanical strength; however, the addition of polymer increases the viscosity of the matrix, which affects redox mediator diffusion in DSSCs. In addition, large amounts of polymer in the electrolyte prevent deep penetration of the electrolyte into the mesoporous structure of the semiconductor layer, resulting in defect formation on the interfacial contact between the electrolyte and the dye-adsorbed semiconductor layer. Therefore, a new solid or quasi-solid electrolyte with

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improved conductivity is required. One candidate is a physical gel created by the self-assembly of triblock copolymers in RTIL, which can be achieved by the addition of a small amount of triblock copolymers [19,20].

In this work, we investigated the effect of ion-gel electrolytes formed by the simple addition of poly(styrene-block-ethylene oxide-block-styrene) (SEOS) triblock copolymer to 1-propyl-3-methylimidazolium iodide (PMII), which has been widely used in DSSCs due to its high conductivity. In addition, PMII is known to interact with poly(ethylene oxide) (PEO), which is the central polymer moiety of the SEOS triblock copolymer [21]. Compared to conventional polymer gels, which require 10–30 wt% polymer to form gels [18], much less triblock copolymer is required for ion-gel formation (ca. 5 wt%). This small amount of triblock copolymer maintains the high ionic conductivity of PMII and improves the penetration of the ion-gel electrolyte into the mesopores of the TiO_2 layer, which provides large interfacial contact area between the electrolyte and the dye. To improve the performance of DSSCs, a well-defined structural material, dendron, was used to form an insulating layer, which effectively shields the back electron transfer from the TiO_2 conduction band to I_3^- [22]. The effect was confirmed by photovoltaic characterization.

2. Experimental methods

2.1. Materials

PMII was purchased from C-TRI, and TiO_2 paste (20 nm, Ti-Nanoxide T/SP), *cis*-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium(II) bis(tetrabutylammonium) (N719 dye) and surlyn film (Meltonix 1170-25, film thickness of 25 μm) were purchased from Solaronix. Conductive fluorine-doped tin oxide (FTO) (TEC8, 8 Ω/□, 2.3 mm) were purchased from Filkington Co. Fifth-generation polyester hydroxyl acetylene bis(hydroxymethyl) propanoic acid dendrons (dendron), I_2, tert-butanol, H_2PtCl_6, Ti(IV) bis(ethyl acetoacetato)-diisopropoxide, iso-propyl alcohol (IPA), 1-methylbenzimidazole (1MB), I_2, n-butanol, and dichloromethane (MC) were purchased from Aldrich Co. Poly(styrene-b-ethyleneoxide-b-styrene)s (SEOS1, Mw = 48,600; SEOS2, Mw = 70,400) were purchased from Polymer Source, Inc. (Canada) and used as received. The PEO weight fractions (f_{EO}) of SEOS1 and SEOS2 were 60%, and 68.8%, respectively.

2.2. Fabrication

The photoelectrode was fabricated by spin-coating Ti(IV) bis(ethyl acetoacetato)-diisopropoxide solution (2 wt% in n-butanol) onto the FTO glass and heating at 450 °C for 30 min. Then a 10-μm-thick TiO_2 layer was deposited over the FTO glass using the doctor-blade method and successive sintering at 450 °C for 30 min using TiO_2 paste. The TiO_2 thin film was dipped in 0.3 mM N719 dye in mixed solvents (1:1 mole ratio of acetonitrile and *tert*-butanol) for 18 h at 30 °C. Then the residual dye solution was rinsed with acetonitrile and dried with N_2 gas. For the treatment of dendron, 100 μl of 0.3 mM dendron solution was dropped onto the top of the dye-dipped cell and dried at room temperature for one day. Then the residual dendron was rinsed with acetonitrile and dried with N_2 gas. The active area of the DSSC was 0.5 cm × 0.5 cm. The Pt counter electrodes were prepared by spin-coating H_2PtCl_6 solution (0.01 M in IPA) onto the conductive FTO glass and successively sintering at 450 °C for 30 min. The Pt counter electrode and the dye-anchored photoelectrode were then assembled into a sealed sandwich-type cell using surlyn film.

The ionic liquid electrolyte was prepared by dissolving the appropriate amount of PMII, I_2 and 1MB in MC to form a homogeneous solution. The mole ratio of PMII/I_2/1MB was optimized to be 12:0.5:1. Ion-gel electrolytes were fabricated by dissolving 5 wt% of SEOS1 or SEOS2 copolymer in PMII/I_2/1MB solution in MC. MC was removed by evaporation at room temperature for 24 h, followed by placing the solution in a vacuum oven at 40 °C until a constant weight was achieved [19]. SEOS1 and SEOS2 films were also prepared using the same procedure.

2.3. Characterization

The ionic conductivity of the ion-gel electrolytes was determined using a laboratory-made four-point probe conductivity cell connected to an impedance analyzer (IM6e, Zahner) [23]. The ionic conductivities (σ) of the ion-gels were calculated using the relation $\sigma = L/ZA$, where L is the thickness of the electrolyte (cm), Z is the impedance (Ω) and A is the effective area (cm^2). Wide-angle X-ray diffraction analysis (WAXD) was conducted with a Rigaku, D/MAX RINT 2000 high-resolution diffractometer using Ni-filtered Cu Kα radiation. The scanning angle was varied from 4 to 75° at a scanning rate of 5° min^{-1}. All spectra were measured at ambient temperature. The current–voltage characteristics of the DSSCs were performed under 1-sun illumination (AM 1.5G, 100 mW cm^{-2}) with a Newport (USA) solar simulator (300 W Xe source) and a Keithley 2400 source meter using a mask with an aperture area of 0.36 cm^2. Electrochemical impedance spectroscopy (EIS) was measured with a potentiostat in a frequency range of 100 mHz–1 MHz under forward bias (−0.62 V) in the dark. The cross-section of the cell was examined by field-emission scanning electron microscopy (FE-SEM) (Hitachi S-4700, Japan). IPCEs (PV Measurement Inc.) were measured using a halogen source for monochromatic light and a broadband bias light to approximate the illumination of 1 sun. Raman measurements of the samples were made using a backscattering geometry with a Jobin-Yvon LabRam HR fitted with a liquid-nitrogen-cooled CCD detector. The spectra were collected under ambient conditions using the 514.532-nm line of an argon-ion laser (0.5 mW).

2.4. Computational method

Diethyl ether (DE) was used as the model compound of the PEO moiety of SEOS for simplicity. The electronic energies and structures of the stationary species of interest in the gas phase were calculated by full optimization without any geometrical constraints using the density functional theory method with Gaussian 03 software and Becke's three-parameter hybrid functional (B3LYP) [24] with a 6-31+g(d) basis set [25] for non-metallic elements and the effective core potential of the LANL2DZ basis [25] set for the iodide ion. The nature of all of the species was verified by calculating their vibrational frequencies [26,27]. The charge densities of the complexes were obtained using natural population analysis [28–30].

3. Results and discussion

3.1. Phase-change effect

Ion-gels were formed by the addition of 5 wt% of SEOS1 and SEOS2 to PMII, which can be seen in Fig. 1. It is known that the microphase separation of the solvatophobic styrene moiety at both ends of the SEOS copolymer cause the formation of a gel [19,20].

The WAXD was conducted to deduce the morphological information of SEOS films and PMII/SEOS1 and PMII/SEOS2 ion-gel electrolytes, and the results are shown in Fig. 2a and b, respectively.

The WAXD diffraction patterns of both the SEOS1 and SEOS2 films (Fig. 2a) showed two sharp peaks at $2\theta = 18.3$ and 22.4°, which are consistent with those of the crystalline PEO homopolymer [31].