Short communication

Correlation between ionic conductivity and cell performance in solid-state dye-sensitized solar cells employing polymer electrolyte

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ABSTRACT

Poly(ethylene glycol) dimethyl ether (PEGDME)/fumed silica/1-methyl-3-propyl imidazolium iodide (MPII)/I_2 mixtures were used as polymer electrolytes in solid-state dye-sensitized solar cells (DSSCs). Correlation between the ionic conductivity and cell performance by varying the composition of polymer electrolytes was investigated to elucidate the importance of the ionic conductivity in determining the energy conversion efficiency of solid-state DSSCs. If the ionic conductivity is a rate determining step among many transport processes, the maximum ionic conductivity would match with the best cell efficiency in the solid-state DSSCs. However, the composition with the highest ionic conductivity did not show the maximum solar cell performance, indicating a mismatch between the ionic conductivity and cell performance in these experimental conditions. This suggests that other than the ionic conductivity such as the electron recombination may also play an important role in determining the energy conversion efficiency. Thus, the surface of the TiO_2 particles was modified by coating a thin metal oxide such as Nb_2O_5 layer to prevent electron recombination. As a result, the electrolyte composition of the best cell efficiency was shifted to coincide with that of the maximum ionic conductivity, suggesting that the electron recombination is also important in determining the energy conversion efficiency in addition to the ionic conductivity in solid-state DSSCs.

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1. Introduction

Dye-sensitized solar cells (DSSCs) employing liquid electrolytes have been investigated over the past decades because of their low production cost and high energy conversion efficiency (~11% at 1 sun, AM 1.5) [1–4]. A DSSC configures (1) a photo-electrode with a thin film of mesoporous nanocrystalline TiO_2 particles, where dye molecules are adsorbed, (2) electrolyte containing redox couples such as I^-/I_3^- and (3) a counter electrode commonly coated with a thin Pt or carbon layer. The electricity generation is based on the injection of electrons from the photo-excited state of sensitizer dye molecules into the conduction bands of TiO_2. Thereby, electrons move from the photo-electrode to the counter electrode through an external circuit [1–4].

Liquid state DSSCs having I^-/I_3^- dissolved in a liquid solvent have been studied and demonstrated high energy conversion efficiency. However, leakage, evaporation of solvent and instability of the liquid electrolyte at high temperatures are significant drawbacks to bring DSSCs into the market [5,6]. To overcome these problems, many efforts have been made to replace the liquid electrolyte with solid or quasi-solid media, such as hole transport materials [2,7], ionic liquids [8,9], polymers [5,10,11] and gel electrolytes [12,13]. Polymer electrolytes in particular have good mechanical strength and long term stability, but have low photovoltaic performance due to low ionic conductivity and poor contact between the electrolyte and electrode. Thus, approaches using oligomers have been suggested to improve the efficiency [10,11,14]. Specifically, the preparation of solid-state DSSCs using liquid oligomers, followed by *in situ* self-solidification has been proven to be very effective in improving the energy conversion efficiency, which primarily resulted from increased ion conductivity and enlarged interfacial contact between the dyes and the electrolyte.

Since ionic conductivity of solid-state polymer electrolytes is much low, compared to that of liquid electrolyte, it can be argued whether the correlation between the ionic conductivity and the cell performance can be found. Note that the ionic conductivity in solid-state polymer electrolyte is in the range of 10^{-4} to 10^{-6} S cm^{-1}, whereas that in liquid electrolyte is in the range of 10^{-2} to 10^{-3} S cm^{-1}. If the ionic conduction is the rate determining among many transport processes, the correlation between the ionic conductivity and the cell performance would be expected to be good. In other words, the energy conversion efficiency may be determined significantly by the ionic conductivity in the solid-state DSSCs utilizing polymer electrolytes.

If the correlation is not good, other than the ionic conductivity may also play an important role in determining the energy conversion efficiency in the solid-state DSSCs utilizing polymer electrolytes. In this case, it may be suggested that the electron recombination would also play an important role as in the liquid state DSSCs since it has been known that the recombination process has been known to lower the energy conversion efficiencies [15]. In this work, the correlation between the ionic conductivity and the cell performance will be, therefore, first examined. The importance of the electron recombination in the solid-state DSSCs will also be investigated. Finally, a simple way to improve the energy conversion efficiency will be suggested.

2. Experimental

2.1. DSSC preparation

Solid-state electrolytes were prepared according to the oligomer approach [14]. Composite polymer electrolytes consisting of poly(ethylene glycol) dimethyl ether (PEGDME, $Mw = 500\,g\,mol^{-1}$)/1-methyl-3-propylimidazolium iodide (MPII)/iodine/fumed silica were prepared and solid-state DSSCs according to the following procedure were fabricated [10]. First, polymer electrolytes were prepared by dissolving PEGDME in acetonitrile (ACN), and then various amounts of MPII were added. Specific concentrations of MPII in PEGDME used were 0.95, 1.19, 1.59, 2.03, 2.39, 2.98, 3.29, 3.58, 3.88 and 4.18 M. Iodine was dissolved in the polymer solution at 10 wt% relative to the weight of the MPII, while the silica nanoparticle concentration was fixed at 9 wt% of the total polymer electrolyte. All chemicals were used as received without further purification.

Transparent SnO_2:F-layer conductive glass was used for both the working and counter electrodes. Counter electrodes were prepared by spin coating a H_2PtCl_6 solution (0.01 M in isopropyl alcohol) onto FTO glass and sintering at 450 °C for 30 min. For the working electrodes, a Ti(IV) bis(ethyl acetoacetato)-diisopropoxide solution (2 wt% in 1-butanol) was spin-coated onto FTO glass, followed by heating at 450 °C for 30 min. Then, commercialized nanocrystalline TiO_2 paste (STI 18NR-T) was cast onto the glass using the doctor-blade technique with Scotch tape (3 M) as a spacer, followed by sintering at 450 °C for 30 min. The TiO_2 layers (thickness of TiO_2 layer: 12–13 µm, active area: 0.16 cm²) were then immersed in a $Ru(dcbpy)_2(NCS)_2$ (dcbpy = 2,2-bipyridyl-4,4-dicarboxylato) dye solution (535-bisTBA (N719), Solaronix) in *tert*-butanol and acetonitrile (1:1, v/v) at 30 °C for 18 h. Then, the dye-sensitized TiO_2 film was rinsed with ACN and dried in the dark. A plastic sheet (Surlyn) was inserted between the photo-electrode and counter electrode as the spacer, and the space was subsequently filled with electrolyte. The two electrodes were clipped together and the cells were placed in a 30 °C oven for the evaporation of solvent.

2.2. Ionic conductivity, charge transfer resistance and cell performance

The ionic conductivity of polymer electrolyte with different MPII concentrations was characterized by electrochemical impedance spectroscopy (EIS) using IM6 (Zahner) with a lab-made four probe cell. Polymer electrolytes were introduced in the conductivity measurement cell and dried at 30 °C for over 2 days to remove residual solvent completely. The galvanostatic method was applied and the temperature of conductivity cells was maintained at 30 °C. The frequency range was varied from 1 M to 1 Hz and the amplitude is fixed at 1 µA [10,11]. The conductivity, σ, was obtained from $\sigma = L/ZA$ where L is the thickness of the electrolyte (cm), Z the impedance (Ω) and A the effective area (cm²).

The symmetric cell was employed for the measurement of series or charge transfer resistance (R_{CT}) between the polymer electrolyte and the Pt counter electrode. This cell consisted of two platinized glasses to allow for contact with the electrode and polymer electrolyte. The space in between the electrodes (L) was 50 µm, and this was filled with the electrolyte, resulting in an area (A) of 0.25 cm² [16]. Again, the conductivity cell was connected to an impedance analyzer (IM6, ZAHNER) for measurements [11].

From the current density–voltage (J–V) curves obtained, short-circuit current (J_{SC}, mA cm⁻²), open-circuit voltage (V_{OC}, V), fill factor (FF), and overall energy conversion efficiency (η, %) could be determined using the following definitions:

$$FF = \frac{V_{max} \times J_{max}}{V_{OC} \times J_{SC}}$$

$$\eta\,(\%) = \frac{V_{max} \times J_{max}}{P_{in}} \times 100 = \frac{V_{OC} \times J_{SC} \times FF}{P_{in}} \times 100$$

where P_{in} is the intensity of the incident light (mW cm⁻²).

The photovoltaic performance of DSSCs was measured using a Keithley Model 2400 and a 1000 W xenon lamp (Newport) under AM 1.5 and 100 mW cm⁻². The light intensity (or radiant power) was adjusted with a Si solar cell for 1 sunlight intensity. This intensity was verified with a NREL-calibrated Si solar cell.

2.3. Coating niobium oxide (Nb_2O_5) layer

We also introduced a type of electrode having an intrinsic energy barrier. The conduction and potential difference of Nb_2O_5 is about 100 mV more negative than that of TiO_2 [17]. This potential difference can form an energy barrier at the electrode–electrolyte interface thus reducing the rate of recombination of the photoinjected electrons and improving the collection efficiency. After sintering, the mesoporous TiO_2 films were also coated with at Nb_2O_5 thin layer by spin coating at 2000 rpm for 10 s with a niobium precursor solution (15 mM niobium chloride ($NbCl_5$) in ethanol) followed by oxidation at 450 °C for 30 min [18].

3. Results and discussion

3.1. Influence of MPII concentration on the ionic conductivity and charge transfer resistance

Fig. 1 shows the dependence of the 1-methyl-3-propyl imidazolium iodide (MPII) concentration in the polymer electrolyte on
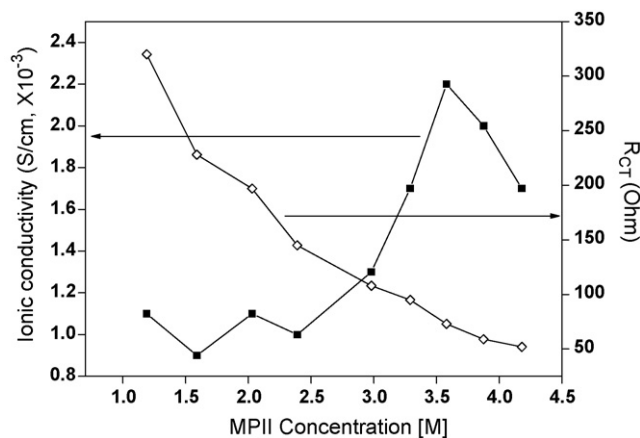

Fig. 1. Ionic conductivity and charge transfer resistance (R_{CT}) for solid-state polymer electrolyte with various concentrations of 1-methyl-3-propylimidazolium iodide (MPII) [M]; PEGDME/MPII/I_2/fumed silica at 30 °C.
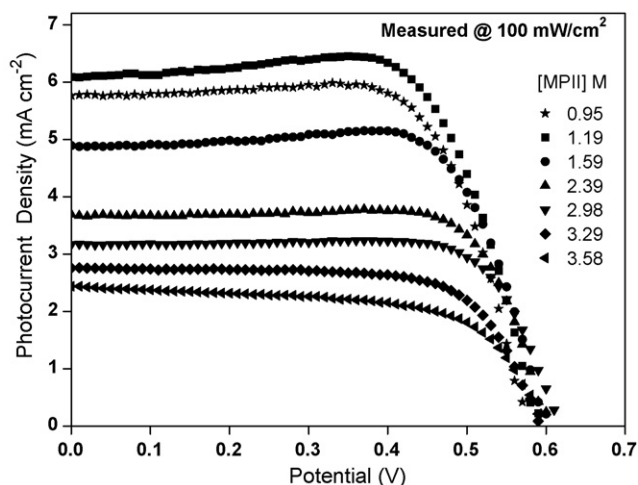
Fig. 2. Photocurrent density–potential characteristics of DSSCs with various concentrations of 1-methyl-3-propylimidazolium iodide (MPII) [M].
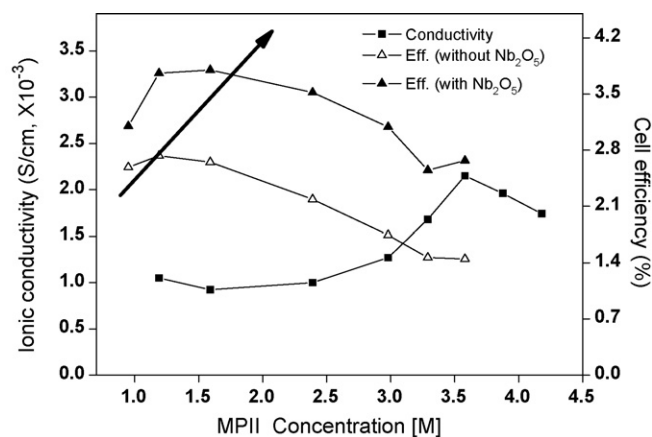

Fig. 3. Ionic conductivity and efficiency with and without a Nb_2O_5 layer as a function of the concentration of 1-methyl-3-propylimidazolium iodide (MPII) [M] (ionic conductivity measured at 30 °C; efficiency measured under 100 mW cm^{-2}, active area: 0.16 cm^2, TiO_2 thickness: 12 μm).

the ionic conductivity and charge transfer resistance at 30 °C. Maximum ionic conductivity of about 2.2×10^{-3} S cm^{-1} was obtained at the MPII concentration of 3.58 M in PEGDME. The initial increase in the ionic conductivity is attributed to the build up of charge carriers [19]. A further increase in the MPII concentration resulted in a decrease in the ionic conductivity due to the formation of ion pairing which reduced the mobility of the ions and the increased viscosity [20].

Charge transfer resistance (R_{CT}) decreased steadily with increasing MPII concentration (i.e., the semicircle diameter decreased in the Nyquist diagram.). This is because the amount of I_3^- ions increased with increasing the MPII concentration, resulting in the faster reduction reactions at the interface between the electrolyte and Pt electrode.

3.2. Photovoltaic performance of DSSCs employing polymer electrolyte

The photocurrent versus voltage curves of the fabricated solar cells as a function of the concentration of 1-methyl-3-propylimidazolium iodide (MPII) are shown in Fig. 2, and the photovoltaic properties are listed in Table 1. The open-circuit voltage (V_{OC}) is similar in all cases, but the short-circuit current (J_{SC}) changed significantly depending on the MPII concentration.

Fig. 3 shows the ionic conductivity and the cell efficiency as a function of the concentration of MPII. The maximum ionic conductivity of the solid electrolytes was obtained with the electrolyte containing 3.58 M MPII in PEGDME, while the highest efficiency and short-circuit current density were obtained with the electrolyte containing 1.19 M MPII. The composition of polymer electrolytes yielding the maximum ionic conductivity did not show the best

Table 1
Photoelectrochemical data of the DSSCs fabricated by varying MPII concentration in the polymer electrolytes.[a].

[EG]:[MPII]:[I$_2$]	Mole ratio (MPII in PEGDME)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	Eff. (%)
10:0.4:0.04	0.95	0.62	8.03	0.63	3.10
10:0.5:0.05	1.19	0.62	9.64	0.63	3.82
10:0.67:0.067	1.59	0.63	9.12	0.67	3.80
10:1:0.01	2.39	0.64	7.99	0.66	3.52
10:1.25:0.125	2.98	0.65	6.31	0.76	3.09
10:1.38:0.138	3.29	0.63	5.66	0.72	2.55
10:1.5:0.15	3.58	0.65	5.22	0.79	2.67

[a] The fumed silica content was fixed at 9 wt% of PEGDME with active area of 0.16 cm^2 and TiO_2 thickness of 12 μm.

solar cell performance, indicating a mismatch between the ionic conductivity and the cell performance. This suggests that the ionic conductivity may not be the rate controlling step among various transport processes in determining the cell efficiency under these experimental conditions, whereas other than the ionic conductivity such as the electron recombination might play an important role in the solid-state DSSCs employing polymer electrolyte.

The short-circuit current (J_{SC}) of the solar cell strongly depends on the ionic conductivity of the electrolyte, i.e., the mobility of I^-/I_3^- redox couple. With increasing the MPII concentration, the ionic conductivity of the electrolyte increased whereas the viscosity of the electrolyte also increased simultaneously. This result induced a decrease in the mobility of I^-/I_3^- redox couple at high concentrations of MPII, resulting in the lower short-circuit current of the solar cell. Based on this, the short-circuit current of the cell reaches a maximum at 1.19 M of MPII.

3.3. Influence of Nb_2O_5 on cell performance as a function of the concentration of MPII

The importance of the electron recombination in determining the energy conversion efficiency was examined in the solid-state
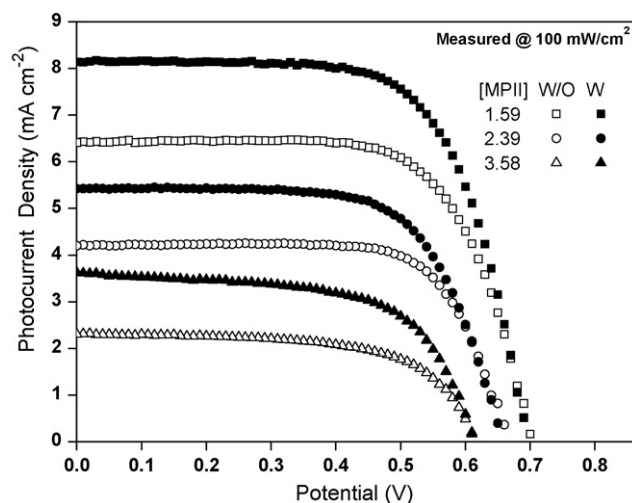

Fig. 4. Photocurrent density–potential characteristics of DSSCs employing polymer electrolyte of PEGDME/MPII/I$_2$/fumed silica with (filled) and without (open) a Nb_2O_5 layer by varying the concentration of MPII [M] (active area of 0.09 cm^2, and TiO_2 thickness of 6 μm).

Table 2
Photoelectrochemical data of the DSSC with and without a Nb_2O_5 layer on the TiO_2 layer.[a]

[EG]:[MPII]:[I_2]	Mole ratio (MPII in PEGDME)	Nb_2O_5	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	Eff. (%)
10:0.67:0.067	1.59	Without	0.70	6.41	0.68	3.07
		With	0.70	8.14	0.67	3.81
10:1:0.1	1.39	Without	0.67	4.20	0.71	2.00
		With	0.66	5.43	0.67	2.39
10:1.5:0.15	3.58	Without	0.62	2.31	0.63	0.90
		With	0.61	3.63	0.62	1.37

[a] The fumed silica content was fixed at 9 wt% of PEGDME with active area of 0.09 cm^2 and TiO_2 thickness of 6 μm.

DSSCs. Fig. 4 shows the current density–voltage ($J–V$) characteristics of the DSSCs with 6 μm TiO_2 films coated by Nb_2O_5; further information is provided in Table 2. When the TiO_2 layer was coated with a thin layer of Nb_2O_5 (ca. 2–3 nm thickness), improved cell efficiencies over the whole range of the MPII concentration were shown. Again, the open-circuit voltage (V_{OC}) remained almost constant, but the short-circuit current (J_{SC}) increased from 6.41 to 8.14 mA cm^{-2} at 1.59 M of MPII under the 1 sun condition and 0.09 cm^2 of active area. At the same time, the energy conversion efficiency also increased from 3.07 to 3.81%. The improved cell performance is attributed to the energy barrier formed by the coating of the new Nb_2O_5 layer. We believe that this is due to the decrease of the recombination rate of the photoinjected electrons in the TiO_2 layer with the oxidized dye and triiodide ion in the electrolyte.

Further, by employing the Nb_2O_5 layer, the correlation between cell efficiency and ionic conductivity was improved as shown in Fig. 3. These results may demonstrate that the energy conversion efficiency in the solid-state DSSCs can be strongly influenced by both the ionic conductivity and the electron recombination.

4. Conclusions

Ionic conductivity of solid-state polymer electrolytes is much low, compared to that of liquid electrolyte. If the ionic conduction is the rate determining among many transport processes, the correlation between the ionic conductivity and the cell performance would be good. However, the mismatch between the ionic conductivity of polymer electrolyte and the cell performance in solid-state DSSCs was found. This suggests that other than the ionic conductivity such as the electron recombination may also play an important role in determining the energy conversion efficiency. On the basis of the suggestion, the surface of the TiO_2 layer was modified by coating nanothin Nb_2O_5 layer on the TiO_2 layer to prevent the electron recombination, resulting in the improvement in the correlation. Therefore it can be concluded that the cell efficiency was strongly influenced by the electron recombination in addition to the ionic conductivity in the solid-state DSSCs employing polymer electrolyte.

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