Effect of ultra-thin polymer membrane electrolytes on dye-sensitized solar cells

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Abstract

In-situ ultra-thin porous poly(vinylidene fluoride-*co*-hexafluoropropylene) P(VDF–HFP) membranes were prepared by a phase inversion method on TiO_2 electrodes coated with Ru N-719 dye. These membranes were then soaked in the organic liquid electrolyte to form the in-situ ultra-thin porous P(VDF–HFP) membrane electrolytes. Dye-sensitized solar cell (DSC) using the membrane electrolyte exhibited an open circuit voltage (V_{oc}) of 0.751 V, a short circuit current (J_{sc}) of 16.260 mA cm^{-2} and a fill factor (FF) of 0.684 under an incident light intensity of 1000 W m^{-2} yielding an energy conversion efficiency (η) of 8.35%. The V_{oc}, FF and η of the solar cell using the membrane electrolyte increased by about 5.8%, 2.2% and 5.7%, respectively, when compared with the corresponding values of a cell using liquid electrolyte. However, the J_{sc} decreased by about 2.1%.

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membrane; polymer membrane electrolyte; P(VDF-HFP); quasi-solid DSCs.

1. Introduction

Photovoltaic technology utilizing solar energy has received considerable attention as one of the environmentally sustainable energy technologies. The dye-sensitized solar cells (DSCs) provide a promising alternative to conventional p–n junction photovoltaic devices because of their relatively high efficiency, simple fabrication process and low production cost [1-3].　The highest efficiency of DSC reported is 11.18% under AM 1.5 ($1000W$ m^{-2}) when used in conjunction with a liquid electrolyte containing the I^-/I_3^- redox couple [4]. However, the liquid electrolyte containing I^-/I_3^- redox couple may limit device stability due to a loss of the iodine by sublimation and the liquid electrolyte may leak or evaporate when the cell is imperfectly sealed. In addition, a permeation of water or oxygen molecules and their reaction with the electrolyte may worsen the cell performance. Liquid electrolyte also makes the manufacture of multi-cell modules difficult [5-7].

Several approaches have been used to overcome such problems by replacing of the volatile liquid electrolyte with a solid-state hole conductor, quasi solid-state gel electrolyte or ionic liquid electrolyte (IL) [5-12]. However, the efficiencies of DSCs with these alternative media are usually lower than that of DSCs with organic liquid electrolyte, which is attributed to a higher ionic transport resistance of such media compared with that of liquid electrolyte. Thus, reducing the ionic transport resistance is a key point to improve the efficiency of DSCs. Recently, DSCs with P(VDF-HFP)/TiO_2

composite electrolyte showed a higher efficiency than that of DSCs with liquid electrolytes, which is due to a low ionic transport resistance and scattering effect [13-14]. On the other side, reduce the thickness of electrolyte can also reduce the ionic transport resistance. Although many gel polymer electrolytes have been reported as alternative electrolytes for DSCs, to our knowledge the use of ultra-thin porous polymer membrane electrolytes has not been reported.

P(VDF-HFP) is a copolymer consisting of crystalline vinylidene fluoride (VDF) and amorphous hexafluoropropylene (HFP) units. It has been widely used as the polymer matrix material in the polymer electrolyte of lithium rechargeable battery due to its excellent chemical stability and mechanical properties [15-16]. The application of a thin film of poly(methylsiloxane) on exposed TiO_2 surface to passivate the TiO_2/solution interface and thereby reduce an interfacial charge recombination reactions with a ferrocene/ferrocenium redox couple has been reported [17]. Similarly the traps which act as charge recombination centers of the TiO_2 electrode can be covered by the P(VDF-HFP) chains, which is beneficial to reduce the charge recombination rate and improve the efficiency. This paper describes a development of in-situ ultra-thin porous P(VDF–HFP) membrane electrolytes and a comparison of its role in the DSC performances with that of the standard liquid electrolyte.

2. Experimental section

2.1. Preparation of dye-sensitized TiO_2 electrode

TiO$_2$ electrodes were prepared by a spray pyrolysis deposition technique using a mixture of two TiO$_2$ colloids at 150 °C [18]. The mixed TiO$_2$ colloid solution contained TiO$_2$ colloid (TAYCA TKC-302, 25 ml), acetic acid (5.5 ml), TiO$_2$ powder (Degussa P25, 0.5 g) and a non-ionic surfactant (Triton-X-100, 5 drops). The plates were heated at 500 °C for 30 minutes in air and then soaked in a 5×10^{-4} M solution of the Ru N-719 dye, cis-bis(thiocyanato)-N-bis(4,4'-tetrabutylammonium' hydrogen dicarboxylato-2,2'-bipyridine) ruthenium(II) in *tert*-butyl alcohol / acetonitrile (1:1, v/v) mixed solution for 12 h.

2.2. Preparation of the electrolyte

P(VDF-HFP) copolymer (Aldrich) was dissolved in acetone and ethanol (4:1, v/v) mixed solvent and its weight percentage was 0.4%. The in-situ ultra-thin porous P(VDF–HFP) membranes were prepared by using (membrane I) one drop, (membrane II) two drops or (membrane III) four drops of P(VDF-HFP) acetone/ethanol solution on the TiO$_2$ electrodes coated with Ru N-719 dye. The TiO$_2$ electrode with P(VDF–HFP) membrane was kept in a vacuum at room temperature for 0.5 h and then soaked in the liquid electrolyte (0.1 M LiI, 0.05 M I$_2$, 0.5 M *tert*-butyl pyridine, 0.6 M 1,2-dimethyl, 3-propylimidazolium iodide in acetonitrile) to form the in-situ ultra-thin porous P(VDF–HFP) membrane electrolyte.

2.3. Fabrication of the DSCs

The TiO$_2$ electrode with P(VDF–HFP) membrane electrolyte was covered with a Pt sputtered counter electrode to complete the cell. An identical solar cell with the organic liquid electrolyte was also assembled for comparison purposes.

2.4. Measurements

For the scanning electron microscopy (SEM) experiment, TiO$_2$ electrode was sputter coated with gold for 40 seconds at a current of 7 mA. A SEM (JEOL 6320F) instrument with an accelerating voltage of 15 kV was employed to examine the TiO$_2$ electrode surface, and in-situ ultra-thin porous P(VDF–HFP) membranes were examined without gold coating with an accelerating voltage of 2 kV. Because the surface of TiO$_2$ electrode is rough, it is difficult to measure the thickness of the in-situ ultra-thin porous P(VDF–HFP) membranes on TiO$_2$ electrodes directly. For the measurement of thickness, these membranes were formed on the FTO glass by using one, two or four drops of P(VDF-HFP) acetone/ethanol solution on the FTO glass to obtain membranes I, II and III as described above. The thicknesses of the above membranes were measured using an optical microscope (Keyence VK-8510) under a magnification of 2000. I-V characteristics of the cells at AM 1.5 (1000 W m^{-2}) were measured with a calibrated JASCO CEP-25 BX solar cell evaluation system. The solar simulator lamp was calibrated with an Eko-LS-100 spectroradiometer and a standard silicon diode. The voltage sweeping time was 20 mV/s and the scanning range was from -0.2 V - 0.8 V. The area of the cell exposed to light was 0.25 cm^2.

3. Results and discussion

3.1. Morphology of the in-situ ultra-thin porous P(VDF–HFP) membranes

Fig. 1 (a) shows the SEM micrographs of TiO_2 electrode coated with Ru N-719 dye, while (b), (c) and (d) show the SEM micrographs of membranes I-III covered on the TiO_2 electrodes coated with Ru N-719 dye, respectively. TiO_2 electrode coated with Ru N-719 dye is composed of nanosized TiO_2 particles and the surface is rough. Membranes I-III cover the TiO_2 electrodes uniformly and their surfaces are much smoother than that of bare TiO_2 electrode coated with dye. With the increase of the membrane thickness (Table 1), the roughness of the membrane was reduced, while the number of pores was decreased.

3.2. Photocurrent characteristics

Fig. 2 shows I-V characteristics of TiO_2 DSCs employing liquid electrolyte and in-situ ultra-thin porous P(VDF-HFP) membrane electrolytes under AM 1.5 radiation (1000 W m^{-2}), and I-V parameters of cells with varying thicknesses of the membrane electrolytes are summarized in Table 1. Compared to a DSC with the standard liquid electrolyte, DSCs with in-situ ultra-thin porous P(VDF-HFP) membrane electrolytes have higher V_{oc} values. This is probably related to the suppression of charge recombination at the interface between the electrolyte and the TiO_2 surface.

In a DSC, the dye absorbs the solar radiation and then injects its electron into the conduction band of the TiO_2 semiconductor. In TiO_2 particles, there are many trap states and some of these are Ti(III) states resulting from the localization of an electron in the Ti 3d orbital in the presence of an electron donating defect (oxygen vacancies, surface

binding and intercalation of cations, proton insertion). Electrons trapped by these states leave traps by thermal activation to the conduction band and then diffuse in the conduction band until they are trapped again. When an electron reaches a trap adjacent to an adsorbed cation, recombination takes place [19-21].

Because the TiO_2 can be considered as a Lewis acid and P(VDF-HFP) containing the fluoride chains as a Lewis base, Lewis acid–Lewis base interactions can exist between the TiO_2 surface and P(VDF-HFP) chains. When the in-situ ultra-thin P(VDF–HFP) membrane electrolyte is formed on a TiO_2 electrode, the surface of TiO_2 electrode gets covered with the P(VDF-HFP) chains, which could cover the trap states of the TiO_2 electrode. This increases the physical separation of the cation from the electrode surface and/or changes the reaction energetics and thus reduces the recombination rate [17]. With the increasing of the thickness of in-situ ultra-thin porous P(VDF–HFP) membrane from membrane I to membrane III, the V_{oc} values did not increase, which indicated that a very thin layer of P(VDF-HFP) copolymer is enough to cover the trap states of the TiO_2 particle network. Furthermore a very thin layer of P(VDF-HFP) copolymer is effective to retard the evaporation of liquid electrolyte, which can improve the long term stability of the DSCs.

The lower J_{sc} of DSC with in-situ ultra-thin porous P(VDF–HFP) membrane electrolyte is due to the increased resistance to ionic conduction compared to that of liquid electrolyte. With increasing thickness of the P(VDF–HFP) membrane, the J_{sc} values of DSC with membrane electrolyte tend to decrease, which is due to the increase

in resistance to ionic conduction. The higher FF observed with the in-situ ultra-thin porous P(VDF–HFP) membrane electrolyte is due to the suppression of the charge recombination at high voltages. With the decrease of the P(VDF–HFP) membrane thickness, the efficiency of DSC with membrane electrolyte was found to increase. DSC with membrane I electrolyte showed the highest efficiency. As compared with the cell using liquid electrolyte, the V_{oc}, FF and η of the solar cell using the membrane electrolyte increased by about 5.8%, 2.2% and 5.7%, respectively. However, the J_{sc} decreased by about 2.1%.

4. Conclusion

DSCs with in-situ ultra-thin porous P(VDF–HFP) membranes showed higher V_{oc} compared with that of DSC with liquid electrolyte. The higher V_{oc} is due to the suppression of charge recombination at the interface between the electrolyte and the TiO$_2$ surface. A very thin layer (150 ± 50 nm) of P(VDF-HFP) copolymer is enough to cover the trap states of the TiO$_2$ electrode and increase the physical separation of the cation from the electrode surface and/or change the reaction energetics and thus reduce the recombination rate. Furthermore, a very thin layer of P(VDF-HFP) copolymer is effective to retard the evaporation of liquid electrolyte, which can improve the stability of the DSCs. DSC with the membrane I electrolyte exhibited the highest efficiency of 8.35%.

Acknowledgments

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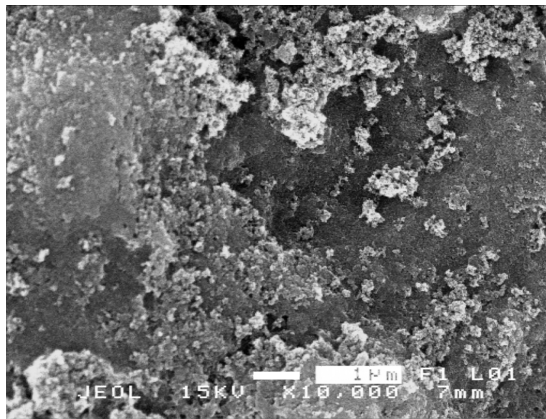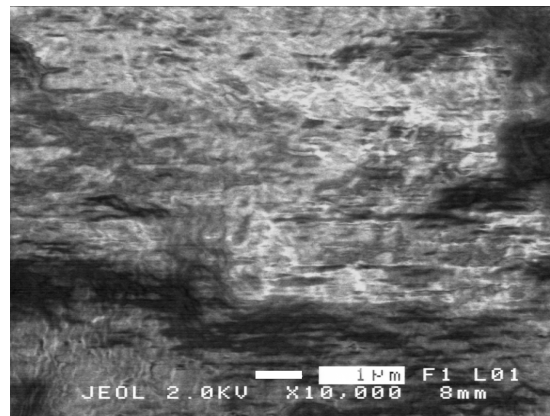
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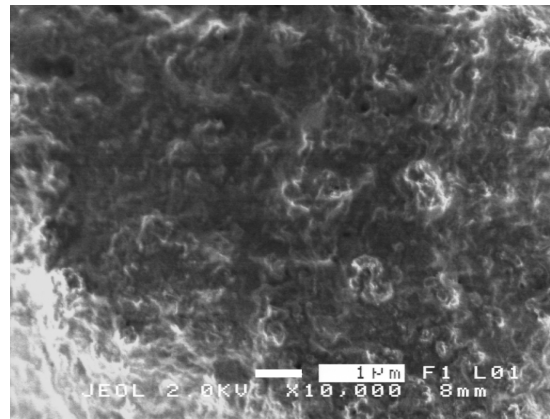
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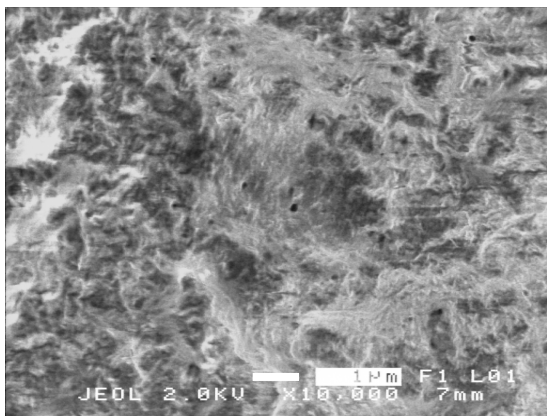
(c)

(d)

Fig. 1. SEM micrograph of (a) (No membrane) the TiO_2 plate coated with dye and in-situ ultra-thin porous P(VDF–HFP) membranes prepared by using (b) (Membrane I) one drop, (c) (Membrane II) two drops and (d) (Membrane III) four drops of 0.4wt% P(VDF-HFP) acetone/ethanol solution on TiO_2 plate coated with dye. The scale bar is 1 μm.
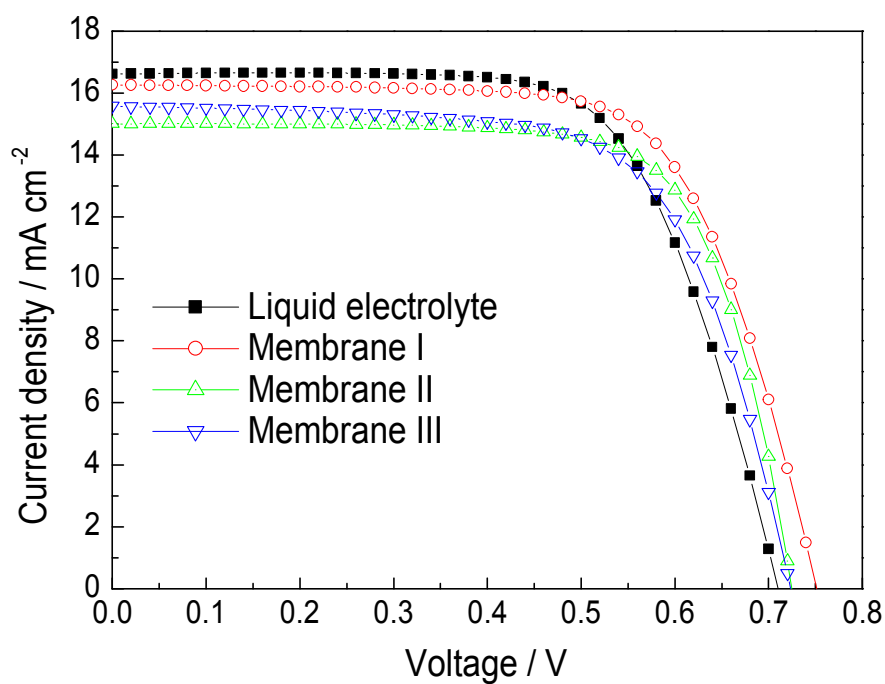
Fig. 2. Photocurrent-voltage curves obtained for TiO_2 DSCs employing liquid electrolyte and in-situ ultra-thin porous P(VDF–HFP) membrane electrolytes under AM 1.5 radiation (1000 W m^{-2}). The liquid electrolyte had the following composition: 0.1 M LiI, 0.05 M I_2, 0.5 M *tert*-butyl pyridine, 0.6 M 1,2-dimethyl, 3-propylimida- zolium iodide in acetonitrile.

Table 1

Photovoltaic performance of TiO$_2$ DSCs employing liquid electrolyte and in-situ ultra-thin porous P(VDF–HFP) membrane electrolytes with different thicknesses of the membranes under AM 1.5 radiation (1000 W m^{-2}). The liquid electrolyte had the following composition: 0.1 M LiI, 0.05 M I$_2$, 0.5 M *tert*-butyl pyridine, 0.6 M 1,2-dimethyl, 3-propylimida- zolium iodide in acetonitrile.

	V_{oc}(V)	J_{sc} (mA cm^{-2})	FF	η(%)	Thickness (nm)
Liquid	0.710	16.612	0.669	7.90	
Membrane I	0.751	16.260	0.684	8.35	150±50
Membrane II	0.725	15.006	0.720	7.83	350±50
Membrane III	0.723	15.580	0.669	7.54	650±50