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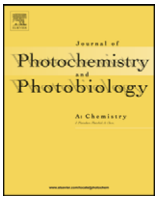

Dye-sensitized solar cells containing polymer film with honey-comb like morphology

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ABSTRACT

Flat membranes with honey-comb like morphology were prepared on dye coated TiO_2 electrode. Liquid electrolytes were immobilized in the pores of the honey-comb like structure of the polymer membranes due to high capillary force. The liquid impregnated polymer membranes were introduced to dye-sensitized solar cells (DSSCs), forming quasi-solid-state electrolytes for highly efficient DSSCs with an overall energy-conversion efficiency of ~8% at room temperature under 1 sun illumination.

1. Introduction

Dye-sensitized solar cells (DSSCs) have considerable promise for future commercialization due to their high-energy conversion efficiency and low production cost, making them viable alternatives to silicon solar cells [1–3]. At present, however, practical problems such as leakage of liquid electrolyte remain serious obstacles to their application [4]. In this regard, an essential research subject is solidification of the electrolyte. All-solid DSSCs [5–7] and quasi-solid DSSCs [8–10] filled with gel electrolyte have been reported. Polymers are widely used as agents for the solidification of liquid electrolytes [11,12]. However, the conversion efficiencies of the solid-state DSSCs are in most cases much lower than the corresponding liquid DSSCs, possibly due to deteriorated ionic transfer properties after the liquid electrolyte was solidified [12].

Poly(vinylidene)fluoride (PVDF)-based co-polymers are very attractive gelators, exhibiting chemical and mechanical resistances [8]. It is known that fluorinated polymers are photochemically stable even in the presence of TiO_2 and Pt nanoparticles [13]. In a recent study, Wang and co-workers used an ionic liquid polymer gel containing poly(vinylidenefluoride-co-hexafluoropropylene) (PVdF-HFP) and 1-methyl-3-propylimidazolium iodide and confirmed that the photovoltaic performance of polymer gel electrolyte-based DSSCs compared favorably well with liquid electrolyte-based cells [8]. Kang et al. also investigated the effects of PVdF-HFP, a promising gelator, in N-methyl-2-pyrrolidone (NMP) on the photocurrent–voltage characteristics and the stability of DSSCs [14]. However, the mechanical properties of these gel-type electrolytes are not satisfactory for commercialization, and several approaches to close the gap between the gel electrolyte-based DSSCs and all-solid-state DSSCs by the addition of nanoparticles are being investigated [9,15,16]. Wei et al. prepared a PVdF-HFP/PEG/PEGDMA cross-linked film with porous structure as the electrolyte for DSSC [15]. However, their cell performance was not comparable to that of liquid-based electrolyte. Zhang et al. also prepared a porous polymer membrane as a separator for DSSC [17].

In the present work, we describe the preparation of a flat membrane with a honey-comb like morphology directly on a dye-absorbed TiO_2 electrode via a simple dip coating process and its application to a DSSC. Liquid electrolyte is trapped in the pores of the honey-comb like structure, resulting in retardation of leakage of the liquid electrolyte (Fig. 1). Owing to the reduced flow due to the unique morphology and high ion-mobility of the liquid electrolyte, a ~8% efficiency DSSC has been realized, a level similar to that of liquid electrolyte-based DSSCs.

2. Experimental

2.1. Preparation of TiO_2 films

A fluorine-doped SnO_2 conducting glass (FTO) substrate was sonicated in an ethanol and acetone mixture (1:1 volume ratio)

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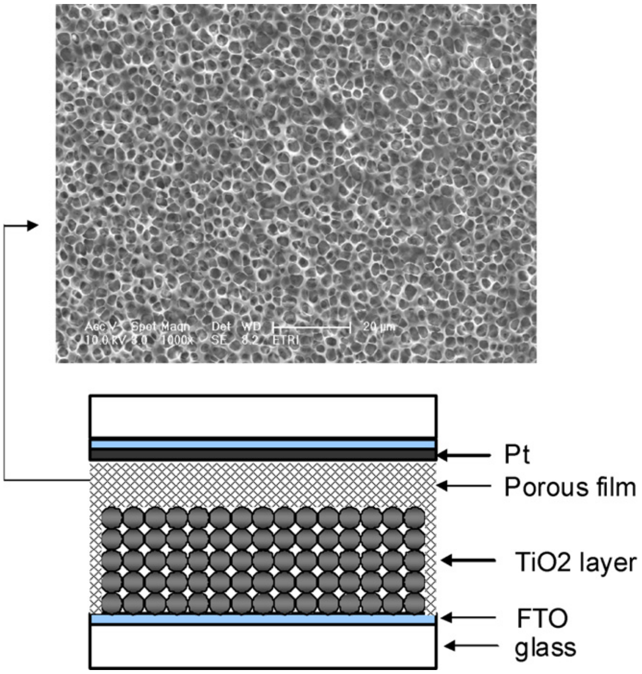

Fig. 1. Film morphology of the PVdF-HFP and configuration of the DSSC.

for 5 min, and then sonicated in a 5% Micro-90 aqueous solution for 5 min. A spin-coating method using 100 mM Ti-isoproxide was applied to form a thin TiO_x underlayer on a FTO glass anatase TiO_2 colloids were made from a sol–gel hydrolysis and autoclaving of titanium isopropoxide at 230 °C for 12 h in an acetic acid aqueous solution, as described elsewhere [18]. TiO_2 nanoparticles were dispersed in α-terpinol with ethyl cellulose as a binder. The solution was applied with a doctor blade to produce a TiO_2 film on the supporting substrate. A 12 μm transparent high surface area layer of 20 nm sized TiO_2 particles was first printed on a FTO electrode, and this layer was subsequently coated by a 5 μm thick second layer of 300 nm light scattering particles.

2.2. Cell fabrications

To coat dye on a TiO_2 film, the samples were immersed in 3×10^{-4} M Ru(II)LL′(NCS)2 (L = 2,2′-bipyridyl-4,4′-dicarboxylic acid, L′ = 2,2′-bipyridyl-4,4′-ditetrabutylammonium carboxylate, Solaronix) ethanol solution for 18 h. For preparation of a porous ~15 μm-thick PVdF-HFP film (Kynar, Powerflex) with a honeycomb like structure, dye-coated TiO_2 electrode was immersed in PVdF-HFP solution in acetone for 1 s and then dried in a chamber under controlled temperature (25 °C) and humidity for 1 min. Counter electrodes were prepared by applying a drop of H_2PtCl_6 on FTO glass followed by heating at 400 °C for 15 min. Single drops of an electrolyte were applied on PVdF-HFP coated TiO_2 electrode. The dye-absorbed TiO_2 electrode with the porous polymer film and Pt counter electrode were assembled into a sealed sandwich-type cell by heating with a hot melt of a polymer film (Surlyn, Dupont 1702, 30 μm). The electrolyte was composed of 0.6 M butylmethylimidazolium iodide, 0.03 M I_2, 0.1 M guanidinium thiocyanate, and 0.5 M 4-tert-butylpyridine in a mixture of acetonitrile and valeronitrile (85:15, v/v). For preparation of DSSC without PVdF-HFP, the dye-absorbed TiO_2 electrode was assembled with Pt counter electrode following same experimental procedure for the DSSC with PVdF-HFP.

2.3. Measurement

The *J*–*V* curves were measured at AM 1.5 illumination using a Keithley 2400 source measure unit. A 1000 W xenon lamp (Oriel, 91193) served as the light source and its intensity was calibrated using a Si reference cell (Fraunhofer ISE, certificate no. C-ISE269). The electrochemical impedance spectra were measured with an impedance analyzer (Solartron Analytical, 1255B) equipped with a potentiostat (Solartron Analytical, 1287) under illumination using a 1000 W xenon lamp. The applied bias voltage and AC amplitude were set at the open-circuit voltage of each DSSC and 10 mV, respectively.

3. Results and discussion

Two different morphologies of PVdF-HFP films were obtained, as shown in Fig. 2. Generally, several parameters such as precipitation temperature and composition of the polymer solution (concentration, type of solvent) affect the morphology of the PVdF-HFP. However, highly porous PVdF-HFP films were readily obtained by controlling the humidity of the atmosphere. The PVdF-HFP was dissolved at room temperature in the solvent acetone at 5 wt.% concentration and then coated on the dye-absorbed TiO_2 electrode under two different humidity levels (15% and 40%). When the film was prepared under a high humidity condition, a very porous PVdF-HFP structure was obtained. The possibility of liquid–liquid de-mixing or crystallization of the polymer film seems to be affected by water molecules in the air [19]. Fig. 2(a and b) shows photographs of two different PVdF-HFP films impregnated with liquid electrolyte. For comparison, Fig. 2(c) shows a photograph of the liquid electrolyte. Fig. 2 indicates that highly porous polymer films could immobilize the liquid electrolyte in a manner resembling solidification of an electrolyte. However, no obvious immobilization of the liquid electrolyte was observed for the non-porous PVdF-HFP film prepared under low humidity. This new concept is useful in better confining the liquid electrolyte in the final cell, thereby possibly improving the lifetime of the cell by preventing failure due to electrolyte leakage. In the DSSC assembled with a porous PVdF-HFP film, the organic solvent containing the $I^-/I_3{}^-$ redox couple is well encapsulated in the pore of a PVdF-HFP film. Moreover, unlike conventional methods to prepare gel-type electrolyte such as solution casting from direct dissolution of the polymer in the electrolyte solution, porous PVdF-HFP film keeps a mechanically robust structure even after the liquid electrolyte is added.

The *J*–*V* curves of the two DSSCs (with and without porous film) were measured at 100 mW/cm^2 and are presented in Fig. 3. The PVdF-HFP thickness was fixed at 20 μm. The maximum energy conversion efficiency was as high as 8.0% at 100 mW/cm^2 for the DSSC employing the porous PVdF-HFP film. More than 10 cells were prepared and tested at the same time. The DSSCs with/without PVdF-HFP show almost same energy conversion efficiency. Although the flow-ability of the PVdF-HFP-based electrolyte is much lower than that of the liquid electrolyte-based electrolyte, the corresponding *I*–*V* curves are practically identical. This indicates that triiodide and iodide can freely move in the open channels of the PVdF-HFP network. The maximum IPCE value was 75% at 540 nm for the PVdF-HFP-based cells, which is comparable to the value obtained for liquid-based DSSCs (Fig. 4).

Fig. 5 depicts the electrochemical impedance spectra for the liquid electrolyte-based cell and PVdF-HFP/liquid electrolyte-based cell. R_o in Fig. 5 is the ohmic resistance of the dye-sensitized solar cells. Electron transport processes of a very short time constant are included. First semicircle is the resistance at the TiO_2/FTO interface, the resistance between TiO_2 particles, and at the interface of the Pt/electrolyte solution [20,21]. In the impedance spectra of the liquid electrolyte-based cell and the PVdF-HFP/liquid

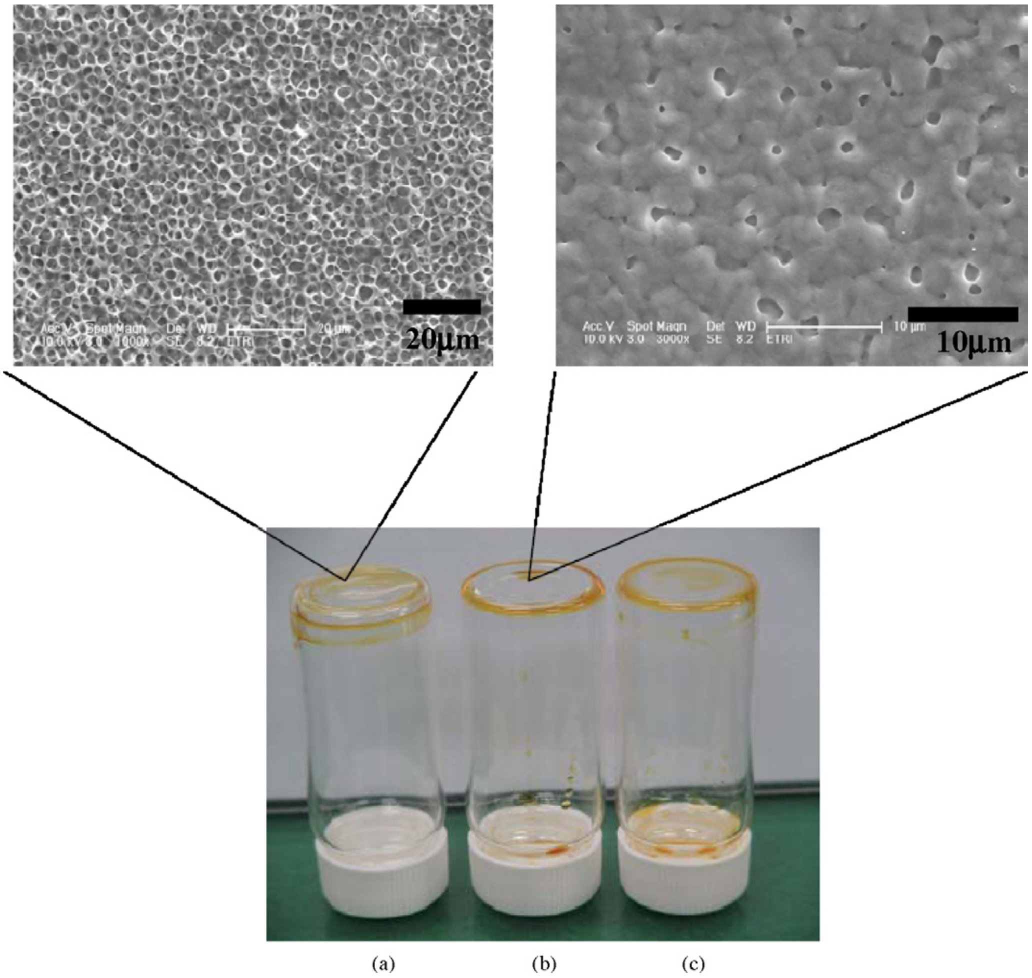

Fig. 2. Photographs of PVdF-HFP films impregnating liquid electrolyte: (a) porous PVdF-HFP film with liquid electrolyte; 2 ml of 5 wt.% PVdF-HFP solution was dried in a chamber under controlled humidity (40%) to prepare porous PVdF-HFP film. Then 0.5 ml of liquid electrolyte was added in the film (b) dense PVdF-HFP film with liquid electrolyte; 2 ml of 5 wt.% PVdF-HFP solution was dried in a chamber under controlled humidity (15%) to prepare porous PVdF-HFP film. Then 0.5 ml of liquid electrolyte was added in the film (c) only liquid electrolyte; 0.5 ml of liquid electrolyte was added in the glass tube.

electrolyte-based cell, first semicircle was almost the same. Second semicircle denotes the resistance at the TiO_2/electrolyte solution and TiO_2/dye interfaces [21]. In our experiments, the resistance in the PVdF-HFP/liquid electrolyte-based cell were slightly larger than those of the liquid electrolyte-based cell, indicating that the PVdF-HFP/liquid electrolyte-based cell has additional resistance at the TiO_2/electrolyte interface or Pt/electrolyte interface due to the additional polymer layer. The response at low frequency is related to the diffusion process of $I^-/I_3{}^-$ redox electrolytes. In the case of

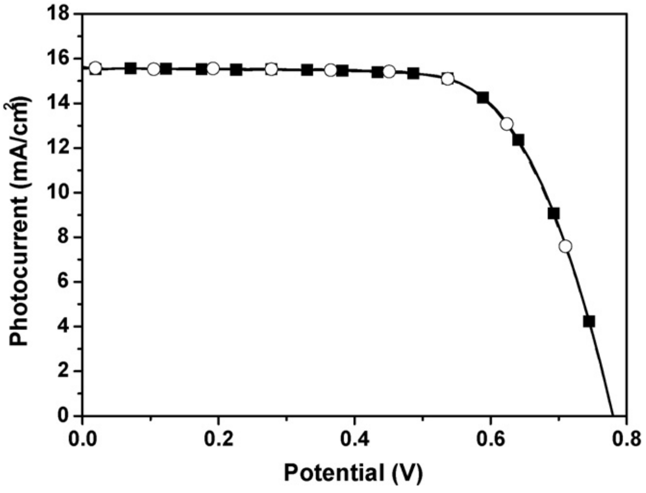

Fig. 3. *J–V* curves of DSSCs with and without porous membrane.

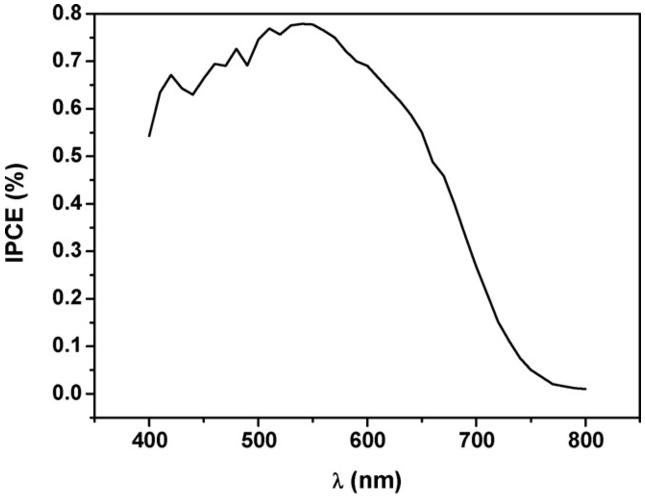

Fig. 4. IPCE spectrum of DSSC with porous polymer film.

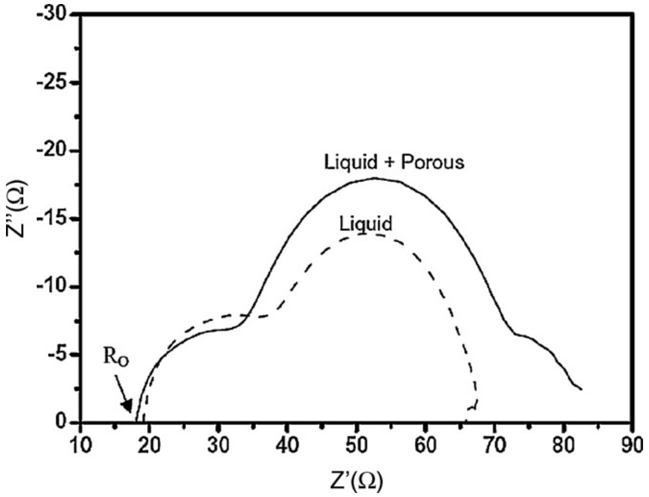

Fig. 5. Electrochemical impedance spectra for DSSCs with and without porous membrane.

the liquid electrolyte-based cell, this component was not observed. However, the PVdF-HFP/liquid electrolyte-based cell also shows an additional semicircle, which represents Nernstian diffusion, arising due to reduced ion-mobility.

Thus far, we have described the efficiency and impedance characteristics of a new system, DSSCs with a porous membrane. The additional porous membrane increased the cell resistance. Nevertheless, cell performance was not hampered by the additional membrane.

4. Conclusions

Flat membranes with honey-comb like morphology were prepared on dye coated TiO_2 electrode. Liquid electrolytes were immobilized in the pores of the honey-comb like structure of the polymer membranes due to high capillary force. The proposed quasi-solid-state DSSC shows energy conversion efficiency that is similar to that of liquid electrolyte-based DSSCs. The present results highlight the promise of commercialization of a new generation of solar cells.

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References

[1] M. Gratzel, Nature 414 (2001) 338.
[2] H. Yang, C. Yu, Q. Song, Y. Xia, F. Li, Z. Chen, X. Li, C. Huang, Chem. Mater. 18 (2006) 5173.
[3] L. Schmidt-Mende, U. Bach, R. Humphry-Baker, T. Horiuchi, H. Miura, S. Ito, M. Gratzel, Adv. Mater. 17 (2005) 813.
[4] M. Gratzel, J. Photochem. Photobiol. A 164 (2004) 3.
[5] B. O'Regan, D.T. Schwartz, J. Appl. Phys. 80 (1996) 4749.
[6] K. Tennakone, G.K.R. Senadeera, D.B.R.A. De Silva, I.R.M. Kottegoda, Appl. Phys. Lett. 70 (2000) 2367.
[7] Y. Saito, N. Fukuri, R. Senadeera, T. Kitamura, Y. Wada, S. Yanagida, Electrochem. Commun. 6 (2004) 71.
[8] D. Chen, Q. Zhang, G. Wang, H. Zhang, J.H. Li, Electrochem. Commun. 9 (2007) 2755.
[9] P. Wang, S.M. Zakeeruddin, P. Comte, I. Exnar, M. Gratzel, J. Am. Chem. Soc. 125 (2003) 1166.
[10] T. Kato, S. Hayase, J. Electrochem. Soc. 154 (2007) B117.
[11] P. Wang, S.M. Zakeeruddin, M. Gratzel, J. Fluorine Chem. 125 (2004) 1241.
[12] M. Li, S. Feng, S. Fang, X. Xiao, X. Li, X. Zhou, Y. Lin, Electrochim. Acta 52 (2007) 4858.
[13] F.R.F. Fan, H.Y. Liu, A.J. Bard, J. Phys. Chem. 89 (1985) 4418.
[14] M.G. Kang, K.M. Kim, K.S. Ryu, S.H. Chang, N.G. Park, J.S. Hong, K.J. Kim, J. Electrochem. Soc. 151 (2004) E257.
[15] T.C. Wei, C.C. Wan, Y.Y. Wang, Sol. Energy Mater. Sol. Cells 91 (2007) 1892.
[16] H. Wang, H. Li, B. Xue, Z. Wang, Q. Meng, L. Chen, J. Am. Chem. Soc. 127 (2005) 6394.
[17] X. Zhang, C.X. Wang, F.Y. Li, Y.Y. Xia, J. Photochem. Photobiol. A 194 (2008) 31.
[18] F. Padinger, C.J. Brabec, T. Fromherz, J.C. Hummelen, N.S. Sariciftci, Opto-electron. Rev. 8 (2000) 280.
[19] T.H. Young, L.P. Cheng, D.J. Lin, L. Fane, W.Y. Chuang, Polymer 40 (1999) 5315.
[20] T. Hoshikawa, M. Yamada, R. Kikuchi, K. Eguchi, J. Electrochem. Soc. 152 (2005) E68.
[21] J. Nemoto, M. Sakata, T. Hoshi, H. Ueno, M. Kaneko, J. Electroanal. Chem. 599 (2007) 23.