

A quasi-solid-state dye-sensitized solar cell based on porous polymer electrolyte membrane

Xiao Zhang^a, Cong-Xiao Wang^a, Fu-You Li^b, Yong-Yao Xia^{a,*}

^a Chemistry Department and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, China

^b Laboratory of Advanced Materials, Fudan University, Shanghai 200433, China

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Abstract

Water was employed as plasticizer to produce porous polymer membrane. The gel polymer electrolyte containing 72% liquid organic electrolyte (0.5 M LiI, 0.05 M I₂, 0.5 M 4-*tert*-butylpyridine in PC) shows ionic conductivity of $6.4 \times 10^{-4} \text{ S cm}^{-1}$ due to its high porous structure. Moreover, the porous electrolyte membrane shows good mechanical strength and serves as a separator in the solar cells. Quasi-solid-state solar cells fabricated with this gel electrolyte displayed energy conversion efficiency of 6.0% when the cell gap was tuned to 30 μm . Moreover, these cells possessed much better long-term stability compared with those based on liquid organic electrolyte.

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1. Introduction

Dye-sensitized solar cells (DSC) have drawn increasing attention in recent years for its lower cost and satisfying efficiency [1–3], however, their application remains limited because their efficiency diminishes quickly due to the leakage of electrolyte. In order to improve their ability of holding the electrolyte, much effort has been devoted to solidify the electrolyte. Inorganic nanoparticle [4–6] and polymer with high molecular weight [7–10] have been employed to solidify liquid electrolyte, yet the quasi-solid-state solar cells employing these kinds of electrolyte exhibit lower efficiency for the comparatively lower ionic conductivity of electrolyte and poor contact performance between electrolyte and the surface of electrode. In the meantime, the poor mechanical strength of electrolyte is disadvantage for the assembly of the cells.

Gel polymer membrane prepared by immersing dry porous polymer membrane in liquid electrolyte has been widely used in Li-ion batteries [11]. Although this kind of gel polymer membrane possesses numerous advantages such as the free-

standing framework, high ionic conductivity and ease of cell fabrication, only very recently this kind of gel polymer membrane was employed to fabricate quasi-solid-state solar cells. In their research, porous polymer membrane based on acrylonitrile-methyl methacrylate co-polymer was prepared with phase inversion method. Gel polymer electrolyte was prepared by immersing porous membrane in organic electrolyte (0.5 M LiI, 0.05 M I₂, 0.5 M 4-*tert*-butylpyridine in CH₃CN). The quasi-solid-state solar cells assembled with this kind of gel polymer electrolyte exhibit solar to energy conversion efficiency of 2.4%; moreover, long-term stability of these cells is superior to those assembled with organic liquid electrolyte [12].

The largest obstacle for the wide application of this membrane is probably its complicated production process [13,14] and lower energy conversion efficiency [12]. Recently porous polymer membrane was produced using water as plasticizer [15]. The resulting membrane possesses outstanding capability of liquid uptaking. Moreover, the preparation process is not only simplified dramatically but also environmentally friendly.

In the present work, we employed this novel method to prepare PVDF-HFP porous polymer membrane using water as plasticizer. Gel polymer electrolyte prepared by immersing the porous membrane in liquid organic electrolyte was employed to assemble quasi-solid-state solar cells. The cell gap was tuned

* Corresponding author. Tel.: +86 21 55664177; fax: +86 21 55664177.
E-mail address: yxia@fudan.edu.cn (Y.-Y. Xia).

by applying porous membranes with different thickness in order to improve the efficiency of solar cells. Thermally sealed cells were applied to test the long-term stability of solar cells based on gel polymer electrolyte and liquid organic electrolyte.

2. Experimental

2.1. Preparation of porous polymer membrane

The dry porous polymer membrane composed of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, Elf Atochem. Kynar Flex 2801 M_w : maximum 477,000 g/mol, minimum 154,000 g/mol) was produced referring to the method described in reference [15]. The plasticizer water at 65 °C was added into the tetrahydrofuran (THF) solution of PVDF-HFP at 65 °C to form a transparent solution. The solution with large viscosity was coated onto glass substrate, on which a thin layer of water was sprayed beforehand with spraygun. Water was sprayed onto the surface of the polymer layer immediately after the process of casting in order to prevent THF from evaporating too quickly. Most of the solvent evaporated in the air at room temperature. Solvent was further removed at 80 °C under vacuum for 24 h.

Round polytetrafluoroethylene (PTFE) molds with diameters of 1.5, 2.5 and 4 cm were employed to control the areas of porous membranes in our experiment. When certain amount of polymer solution was poured into these molds, polymer membranes with different thickness formed. Homogeneous polymer membranes with the thickness of 30–95 μm were prepared conveniently according to this method. Polymer membranes with different weight ratio of $m_{\text{H}_2\text{O}}/m_{\text{polymer}}$ were fabricated for comparison.

The structures of polymer membranes are investigated with scanning electron microscopy (Philip XL30). The gel electrolyte formed after the membrane was immersed in liquid organic electrolyte (0.5 M LiI, 0.05 M I_2 , 0.5 M 4-*tert*-butylpyridine in PC) for a few hours. The resultant electrolyte is freestanding although the composition of liquid electrolyte in the membrane is extraordinarily high.

2.2. Conductivity measurements

The polymer membrane was cut to be round shape with the diameter of 1.4 cm. The thickness of the membrane L was measured with a micrometer. The sample was sandwiched between two pieces of stainless-steel blocking electrodes in the cell, whose structure is shown in Fig. 1. The electrolyte resistance R was measured using a Solartron Instrument model 1287 electrochemical interface and 1255B frequency response analyzer controlled by a computer. The frequency limits were typically set between 1000 KHz and 0.01 Hz. The AC oscillation was 5 mV. The data were analyzed by Zplot software. The ionic conductivity of the membrane σ was then calculated with the equation $\sigma = L/RA$, in which $A = 1.54 \text{ cm}^2$. The temperature dependence of the ionic conductivity was obtained over a range of 0–80 °C.

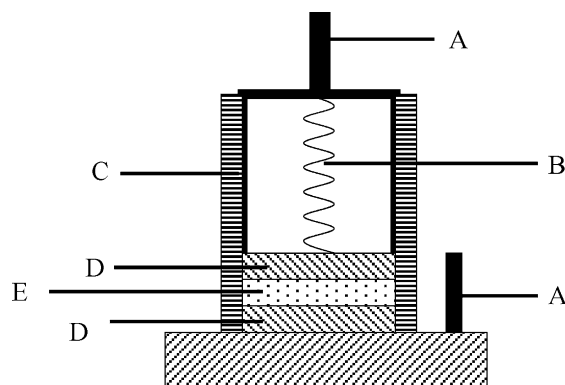


Fig. 1. The components of electrochemical cell for ionic conductivity measurement. (A) Stainless-steel terminals, (B) spring, (C) PTFE cell, (D) stainless-steel blocking electrode and (E) polymer membrane for measurement.

2.3. Mechanical strength measurements

The mechanical properties of the polymer membrane were determined from stress–strain tests using an Instron testing machine (Instron model 5565, Lloyd, UK) at room temperature. All the tests were conducted with a crosshead speed of 50 mm/min. Five specimens of each sample were tested to provide assurance of good reproducibility. The sample dimensions were 35 mm \times 5 mm \times 0.03 mm.

2.4. Fabrication of solar cells

Indium–tin oxide (ITO)-covered glass was used as the substrate of the electrode. TiO_2 paste consisting of photocatalytic TiO_2 powder (Ishihara Sangyo Kaisha Ltd.), PEG400, acetylacetone and distilled water was spread on the glass support by doctor-blade method. After air drying, the electrode was heated to 450 °C at heating rate of 5 °C/min, and then kept at 450 °C for 30 min in air flow. The electrode was immersed in a 0.5 mmol/L solution of *cis*-ruthenium(II)(4,4'-COOH-2,2'-bpy) $_2$ (NCS) $_2$ (N3, solaronix) in dry ethanol for 24 h to absorb dye molecules.

A hole was drilled on platinum counter electrode before the cell was sealed with thermal plastic. The distance between TiO_2 electrode and platinum counter electrode was controlled to be about 35 μm with an adhesive tape to avoid short-circuiting. The liquid electrolyte was introduced into the cell under vacuum. As for the assembly of quasi-solid-state solar cell, gel polymer membranes of different thickness were sandwiched between two electrodes and then applied to measurement. The cell gap can only be roughly controlled by the thickness of gel polymer membranes considering the distortion of the polymer membranes in the cell fabrication process and the thickness of TiO_2 film. The cell performance was evaluated using a Keithley 2400 Source Meter. All experiments were performed at AM 1.5 direct irradiation of 75 mW cm^{-2} light intensity from Oriel 1000 W xenon lamp. The active area of the cell is 0.15 cm^2 . Thermally sealed cells were used to test the long-term stability of the cells. The sealed cells were stored in the oven at 55 °C. These cells were cooled to room temperature and applied to

electrochemical measurement every 24 h in order to study their long-term stability.

3. Results and discussion

3.1. Ionic conductivity of gel polymer electrolyte

The scanning electron microscopic photos of surface and cross section of polymer membranes with weight ratio $m_{\text{H}_2\text{O}}/m_{\text{polymer}}$ of 1.5 are shown in Fig. 2. For comparison, the image for the cross section of polymer membranes produced without water as plasticizer is also included in this figure. According to Fig. 2(b) and (d), the presence of plasticizer affects the morphology of polymer membrane greatly. The membrane produced without plasticizer displays compact structure and no porous structure, while the membrane assisted by water plasticizer shows alveolate structure. The diameters of pores in the porous membrane are about 5 μm . Moreover, the pores are closely interconnected to each other, which make the ion transportation in polymer membrane similar to the behavior in the liquid electrolyte. As is shown in Fig. 2(a), pores on the surface of the membrane display diameters of over 10 μm . It is advantage to hold liquid electrolyte and improve the contact property between electrolyte and electrode. The back contact surface of porous membrane (Fig. 2(c)) also displays porous structure because water was sprayed onto the glass plate beforehand. But the pore distribution in it is not as uniform as the surface of the membrane. The diameters of pores are as large as

20 μm , while some other areas of the back contact surface still display compact structure. The ion transportation in these areas is inevitably blocked.

These two kinds of polymer membranes were immersed into PC organic electrolyte after their weight was measured. The gel polymer membranes were weighed every 20 min. The membrane made without plasticizer contains little organic electrolyte even it is soaked in liquid electrolyte for a few hours. The liquid-holding ability of the porous membrane is extremely high. Its weight increased dramatically during the first hour of the immersion process. After 2 h, the absorption process of organic electrolyte completed, and the liquid electrolyte was not further impregnated into the polymer membrane even though the immersion process was prolonged. Polymer membranes with different $m_{\text{H}_2\text{O}}/m_{\text{polymer}}$ ratio were examined in our experiment. The weight ratio of organic electrolyte in gel electrolyte as well as their ionic conductivity is summarized in Fig. 3. It is shown that the weight ratio of liquid electrolyte in gel electrolyte increases with the increase of amount of plasticizer water. Conductivity of gel electrolyte increases in the meantime. When $m_{\text{H}_2\text{O}}/m_{\text{polymer}}$ reaches 2.5, ionic conductivity of gel polymer electrolyte decreases unexpectedly. It is probably due to the collapse of polymer framework when too much amount of plasticizer is applied.

The mechanical property of the membrane is an important factor for the cell fabrication process. In our experiment, stress–strain measurements were taken on dry and wet porous membrane to investigate the mechanical properties of polymer

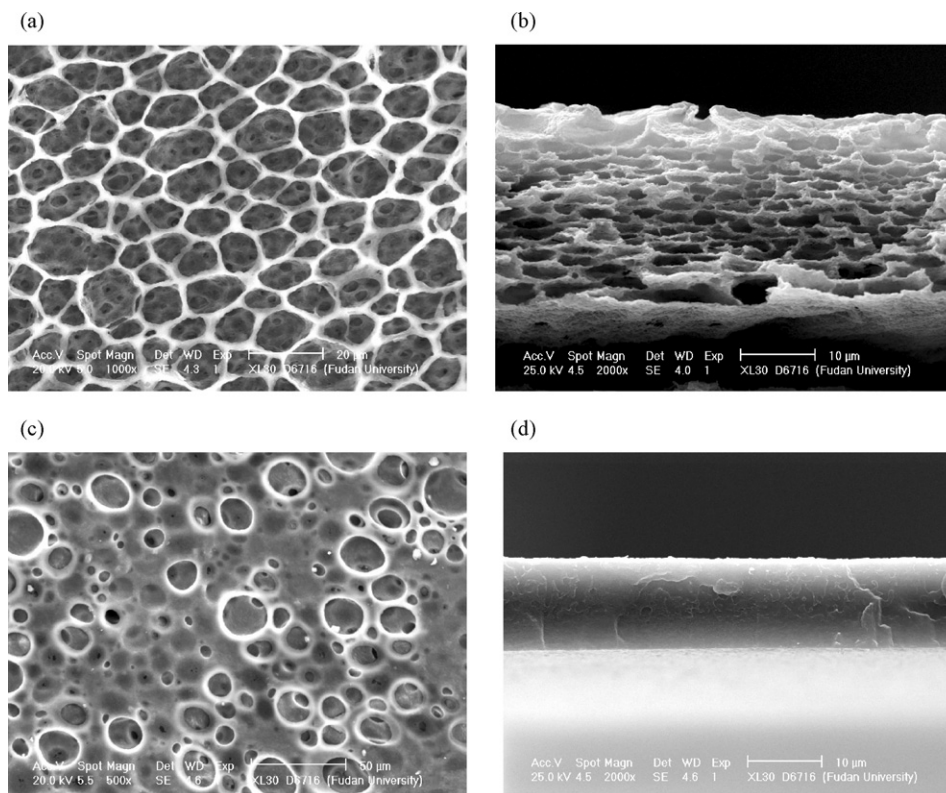


Fig. 2. SEM photos of dry polymer membranes. (a) The top view of polymer membranes with water as plasticizer, (b) the cross-sectional view of polymer membranes with plasticizer, (c) the back contact of polymer membranes with plasticizer. The weight ratio, $m_{\text{H}_2\text{O}}/m_{\text{polymer}}$, is 1.5. (d) The cross-sectional view of polymer membranes without plasticizer.

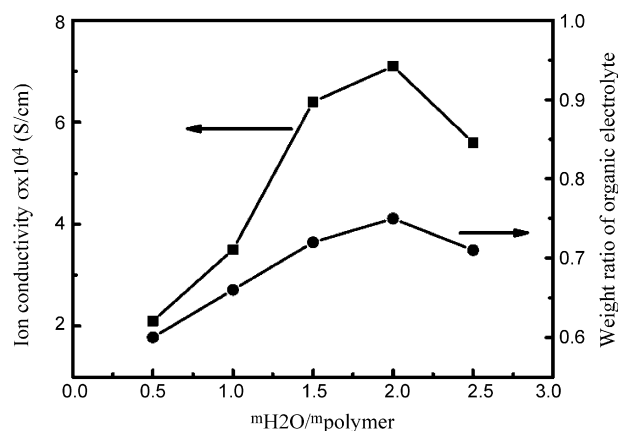


Fig. 3. The ionic conductivity and weight ratio of organic electrolyte of gel polymer electrolyte with different $m_{H_2O}/m_{polymer}$ values.

membrane. The tensile properties of these membranes fabricated with different $m_{H_2O}/m_{polymer}$ values are depicted in Fig. 4, and their mechanical properties are summarized in Table 1. It is shown that the mechanical strength of dry membrane decreases with the increased amount of plasticizer, and the cooperation of PC organic liquid electrolyte in the membrane results in lower tensile strength.

Although the gel polymer electrolyte shows the highest ionic conductivity of $7.1 \times 10^{-4} \text{ S cm}^{-1}$ at the value $m_{H_2O}/m_{polymer}$ of 2.0, but its mechanical strength is relatively poor. Considering both the mechanical strength and ionic conductivity of gel polymer electrolyte to be applied in fabrication of quasi-solid-state solar cells, $m_{H_2O}/m_{polymer}$ value of 1.5 was chosen to prepare porous membrane. Although the weight ratio of liquid electrolyte in the resultant gel polymer membrane is as high as 72%, this gel polymer membrane is still freestanding. The ionic conductivity of the gel polymer electrolyte was determined to be $6.4 \times 10^{-4} \text{ S cm}^{-1}$, whereas the ionic conductivity of PC liquid electrolyte was $6.3 \times 10^{-3} \text{ S cm}^{-1}$ at 298 K. It seems that polymer framework hinders the ion transportation to some extent.

Time-dependented ionic conductivity of gel electrolyte was displayed in Fig. 5. There is no distinct diminishment of its ionic conductivity even it is stored for days, which means organic electrolyte was encapsulated in the pores of the polymer membrane and little liquid leakage took place during this period of storage. The outstanding capability of the porous membrane to hold liquid electrolyte is advantageous to the conservation of ionic conductivity and the sealing of the solar cells. The conductivity-temperature data of PC liquid electrolyte and gel electrolyte are summarized in Fig. 6. It is shown that the ionic conductivity of

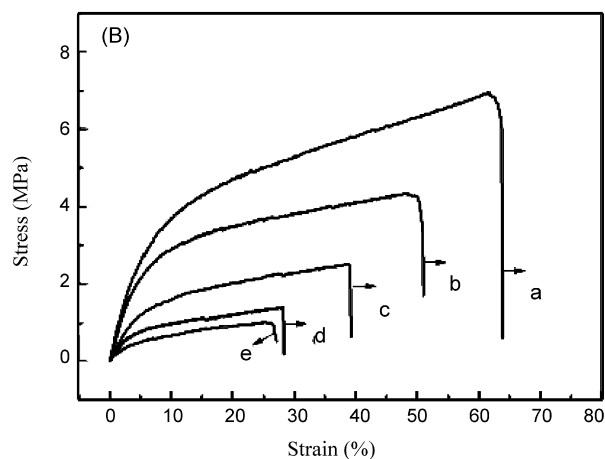
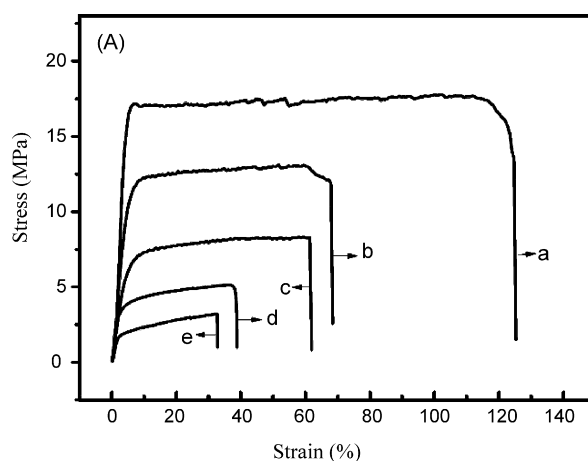


Fig. 4. Stress–strain curves of PVDF-HFP porous membranes with different $m_{H_2O}/m_{polymer}$ values. (a) $m_{H_2O}/m_{polymer} = 0.5$, (b) $m_{H_2O}/m_{polymer} = 1$, (c) $m_{H_2O}/m_{polymer} = 1.5$, (d) $m_{H_2O}/m_{polymer} = 2$ and (e) $m_{H_2O}/m_{polymer} = 2.5$. (A) Dry membranes and (B) wet membranes based on PC organic liquid electrolyte.

gel electrolyte membrane increased more dramatically than that of liquid organic electrolyte as the temperature was increased.

3.2. Photovoltaic performance

The thickness of calcined TiO_2 film is estimated to be $7 \mu\text{m}$, and it is composed of uniform nanoparticles with an average size of 40 nm. The porous structure of the polymer membrane makes the surface of TiO_2 particle contact closely with organic electrolyte in the pores of the membrane, which is advantageous to the charge transfer on the surface of semiconductor particle. Polymer only acts as the framework in this system. It may be evidently predicted that the working mechanism of solar

Table 1
Mechanical properties of PVDF-HFP porous membranes

$m_{H_2O}/m_{polymer}$ Value	Tensile strength (MPa)	Elongation at break (%)	$m_{H_2O}/m_{polymer}$ Value	Tensile strength (MPa)	Elongation at break (%)
Dry state 0.5	17.7	126	Wet state 0.5	7.0	64
1	13.1	68	1	4.4	51
1.5	8.4	62	1.5	2.5	39
2	5.2	39	2	1.4	28
2.5	3.3	32	2.5	1.0	26

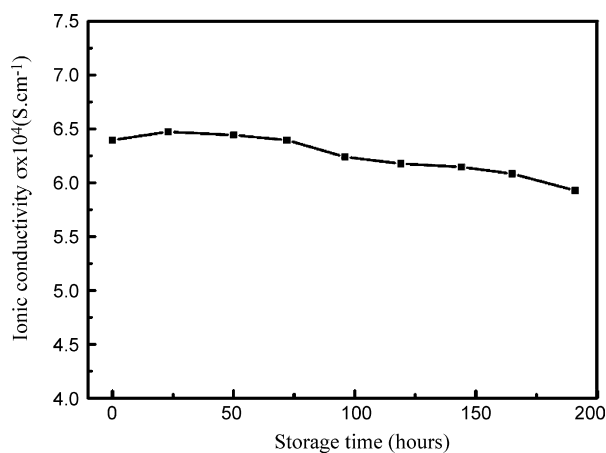


Fig. 5. Ionic conductivity variation of gel polymer electrolyte as a function of storage time at room temperature.

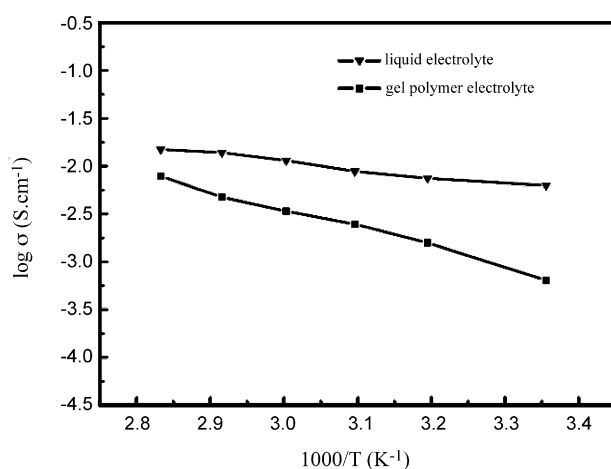


Fig. 6. Arrhenius plot of conductivity-temperature data of PC liquid electrolyte and gel polymer electrolyte.

cells fabricated with this kind of electrolyte should be similar to those employing liquid electrolyte. The cell efficiency with this kind of gel polymer electrolyte should parallel those using liquid electrolyte.

Quasi-solid-state solar cells were fabricated by sandwiching gel polymer membrane between TiO_2 film and counter electrode. The fabrication process is simplified by omitting the liquid polymer filling process and utilization of separator.

Gel polymer membranes with different thickness were employed to fabricate dye-sensitized solar cells. As is shown in Table 2, the ionic conductivity of these membranes is almost independent of their thickness, but the efficiencies of solar cells with them decrease dramatically with the increase of membrane

Table 2

Electrochemical properties of solar cells with different cell gap values (under AM 1.5 illumination 75 mW cm^{-2} , cell active area: 0.15 cm^2)

Cell gap (μm)	V_{oc} (V)	I_{sc} (mA cm^{-2})	ff	η (%)	σ (S cm^{-1})
30	0.72	11.86	0.51	6.0	6.4×10^{-4}
45	0.73	7.82	0.49	4.1	6.3×10^{-4}
95	0.72	5.73	0.45	2.5	5.8×10^{-4}

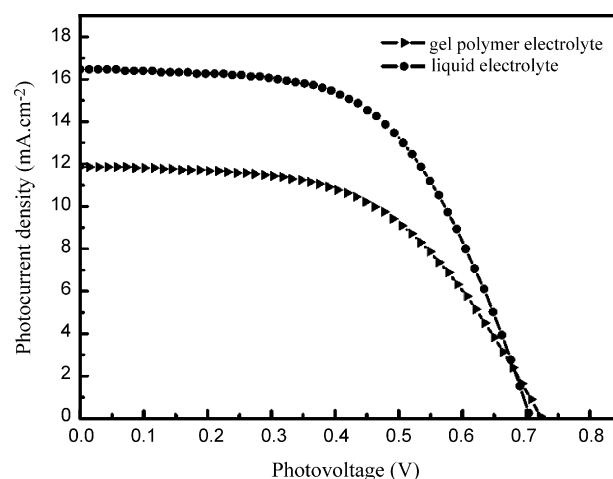


Fig. 7. Photocurrent–voltage curves for dye-sensitized solar cells based on gel polymer electrolyte with the cell gap of $30 \mu\text{m}$ and PC organic liquid electrolyte.

thickness. The solar to energy conversion efficiency η , short circuit current density I_{sc} as well as open circuit voltage V_{oc} and fill factor ff are all demonstrated in Table 2. The I_{sc} value as well as the conversion efficiency diminishes as the cell gap becomes broader, while V_{oc} value remains almost constant until the cell gap increases up to $95 \mu\text{m}$. It is indicated that narrow cell gap is advantageous to high overall conversion efficiency. It is probably due to the fact that solar cells with thick polymer membrane possess higher internal resistance; moreover, it has been elucidated in previous research that the cell gap dependence of cell efficiency is related to the lower diffusion coefficient of I_3^- in gel electrolyte [16]. Further research is requisite in order to elucidate the cause for this phenomenon.

Because too thin polymer membrane is more likely to collapse during the cell fabrication process, gel polymer membrane with the thickness of $30 \mu\text{m}$ was chosen to fabricate solar cells. In DSCs based on liquid electrolyte, cell gap is usually set to be about $35 \mu\text{m}$ in order to avoid short-circuiting [17]. Therefore, the application of gel polymer membrane which serves as a separator in quasi-solid-state solar cells simplifies the fabrication of solar cells.

The photocurrent density–voltage curves for solar cells based on liquid electrolyte (0.5 M LiI , 0.05 M I_2 , $0.5 \text{ M 4-tert-butylpyridine}$ in PC) and gel polymer membrane were summarized in Fig. 7. Their electrochemical properties are all included in Table 3. It is shown that V_{oc} value increases by 0.02 V after gel polymer membrane was applied as the electrolyte, but the I_{sc} value decreases dramatically. As a result, the energy conversion efficiency of the solar cell based on gel polymer membrane decreases to 6.0% compared with the efficiency of 8.6% for the liquid electrolyte. The decrease of efficiency

Table 3

Electrochemical properties of solar cells based on liquid and gel electrolyte (under AM 1.5 illumination 75 mW cm^{-2} , cell active area: 0.15 cm^2)

	I_{sc} (mA cm^{-2})	V_{oc} (V)	ff	η (%)
Liquid electrolyte	16.67	0.70	0.58	8.6
Gel polymer electrolyte	11.86	0.72	0.51	6.0

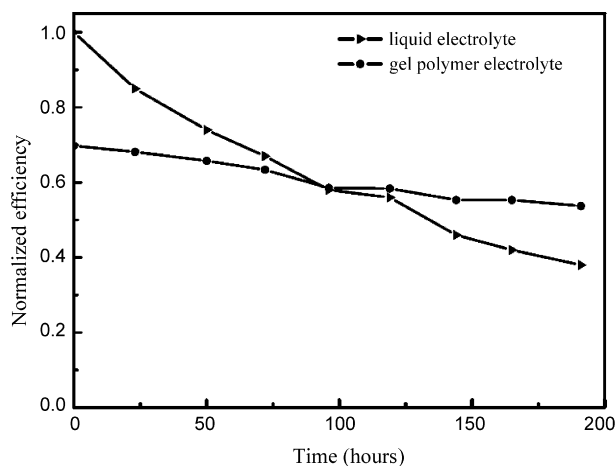


Fig. 8. Normalized device efficiency variation of the dye-sensitized solar cells based on the gel polymer electrolyte and organic liquid electrolyte as a function of storage time.

is probably due to the morphology of the back contact of gel polymer membrane. As is shown in Fig. 2, some areas of the back contact surface still display compact structure. Its ionic conductivity diminishes compared to liquid organic electrolyte due to the hindrance of ion transportation. The interfacial contact property between the surface of polymer membrane and the electrode worsens in the meantime. The preparation technique must be perfected in order to improve the ionic conductivity of gel electrolyte and the interfacial contact property.

3.3. Long-term stability

Gel polymer membranes based on PC organic electrolyte were employed to fabricate quasi-solid-state solar cells. The cells were sealed with thermal plastic tape in order to test the long-term durability of these cells. For comparison, solar cells with PC organic electrolyte were also assembled according to the method described in experimental section. These two kinds of solar cells were stored at 55 °C without any additional protection, and their photocurrent density–voltage curves at ambient temperature were recorded every 24 h. Energy conversion efficiency variances of these cells containing these two kinds of electrolyte are compared in Fig. 8. The efficiency of solar cell with organic liquid electrolyte decreases dramatically due to the leakage of electrolyte, whereas the efficiency of quasi-solid-state solar cell maintains 77% of its initial value. This phenomenon indicates the liquid reserving ability of porous polymer framework is extremely high.

4. Conclusions

Porous polymer membrane was prepared with a novel method by applying water as plasticizer. This method was simplified and

environmentally friendly compared with conventional method such as the phase inversion method. The optimal gel polymer electrolyte containing 72 wt% organic liquid electrolyte delivers a high ionic conductivity of $6.4 \times 10^{-4} \text{ S cm}^{-1}$, and possess good mechanical strength.

The gel electrolyte was employed to fabricate quasi-solid-state solar cells. The energy conversion efficiency of quasi-solid-state solar cells with narrower cell gap of 30 μm reaches 6.0% compared with 8.6% of solar cells with liquid electrolyte. The porous electrolyte membrane also serves as a separator to prevent the DSCs from short-circuiting. The DSCs fabricated with this gel polymer displayed better long-term stability than those with liquid electrolyte. The application of this novel method simplified not only the fabrication of dry porous polymer membrane but also assembly of solar cells. Moreover, this technology made the fabrication of quasi-solid-state solar cells with different shapes more conveniently.

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