

Research Article

New Microporous Polymer Electrolyte Based on Polysiloxane Grafted with Imidazolium Iodide Moieties for DSSC

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Received 26 May 2010; Accepted 16 July 2010

Academic Editor: Canan Varlikli

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Two types of polysiloxane grafted with different ratio of imidazolium iodide moieties (IL-SiO₂) have been synthesized to develop a micro-porous polymer electrolyte for quasi-solid-state dye-sensitized solar cells. The samples were characterized by ¹HNMR, FT-IR spectrum, XRD, TEM and SEM, respectively. Moreover, the ionic conductivity of the electrolytes was measured by electrochemical workstation. Nanostructured polysiloxane containing imidazolium iodide showed excellent compatibility with organic solvent and polymer matrix for its ionic liquid characteristics. Increasing the proportion of imidazolium iodide moieties in polysiloxane improved the electrochemical behavior of the gel polymer electrolyte. A dye-sensitized solar cell with gel polymer electrolyte yielded an open-circuit voltage of 0.70 V, short-circuit current of 11.19 mA cm⁻², and the conversion efficiency of 3.61% at 1 sun illumination.

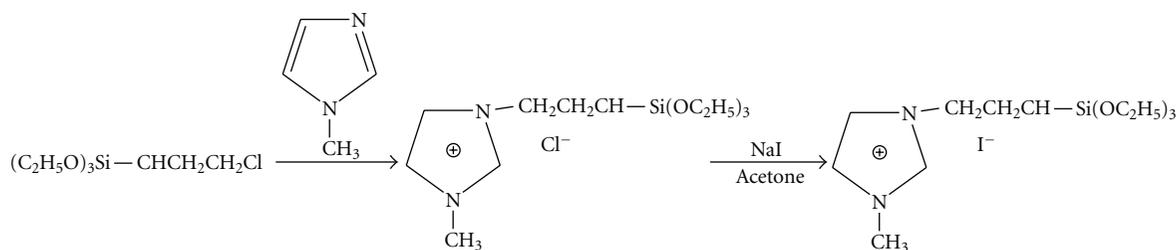
1. Introduction

In recent years, dye-sensitized solar cells (DSSCs) have received much attention because of their high efficiency and low cost [1]. Although liquid electrolyte dye-sensitized solar cells reach power conversion efficiencies of over 11% [2], the main problem is that the liquid electrolytes limit device stability because the liquid may evaporate when the cell is imperfectly sealed, and more generally, the permeation of water or oxygen molecules and their reaction with the electrolytes may worsen cell performance. To solve these problems, alternative robust sealing methods, replacement of the volatile solvents with ionic liquid [3, 4], organic and inorganic hole-transport materials [5, 6], nanocomposites [7, 8], and solid and quasi-solid state polymer electrolytes [9, 10] have been attempted.

Polysiloxanes have highly flexible backbone, with the barrier to bond rotation being only 0.8 kJ mol⁻¹, as well as very low T_g (-123°C) and high free volumes, therefore polysiloxanes-based electrolytes have received much attention. Ren et al. reported a gel network polymer electrolyte based on polysiloxane with internal plasticizing PEO chains applied in solid-state DSSCs. Ethylene carbonate (EC)/propylene carbonate (PC) and LiI/I₂ were added as

liquid plasticizer to improve the performance. The cells showed open circuit voltage of 0.69 V and short-circuit current density of 1.7 mA/cm² under 28 mW/cm² white light illumination. The energy conversion efficiencies and fill factors of the cells were 2.9% [11]. And then a series of novel quaternary ammonium iodides, the polysiloxanes with oligo (oxyethylene) side chains and quaternary ammonium groups, was synthesized in their laboratory. Polymer electrolytes prepared by blending these quaternary ammonium iodides with PEO or PAN were successfully used in fabricating quasi-solid-state DSSCs [12, 13]. Lianos and co-workers have used a nanocomposite silica-based gel with an organic subphase containing propylene carbonate, 1-methyl-3-propylimidazolium iodide, and Triton as surfactant. When applied as electrolyte in DSSCs, it gave a maximum efficiency of 5.4% [14]. The same group achieved an efficiency of 5%-6% with a nanocomposite organic-inorganic sol-gel electrolyte which incorporated a hydrolysable alkoxysilane derivative [15].

However, the polysiloxane-based polymer electrolytes are gums at room temperature rather than solids, and recent efforts have been focused on the design and synthesis of polymers with both high ion transport and good dimensional stability. In our previous paper, a microporous polymer

SCHEME 1: Synthesis of TESPIm⁺I⁻.

electrolyte based on PVDF and ionic liquid functionalized SiO₂ (IL-SiO₂) for DSSCs was reported [16]. The self-standing porous film owns high ambient conductivity and good dimensional stability. And IL-SiO₂ improved the compatibility with liquid electrolyte and polymer matrix for its ionic liquid characteristics. In this paper, we extend our research to investigate the effects of proportion of imidazolium iodide moieties on the conductivities and the cell performances.

2. Experimental

2.1. Polysiloxane Functionalization

2.1.1. Synthesis of Imidazolium Iodide Containing Triethoxysilane Group. The imidazolium iodide type ionic liquid, namely, TESPIm⁺I⁻ was synthesized with Teflon-lined stainless autoclaves under solvent-free conditions (seeing Scheme 1). The mixture of 1-methylimidazolium (75.0 mmol) and 3-chloropropyltriethoxysilane (80.0 mmol) was placed in a 50 mL Teflonline stainless steel autoclave, and then was heated in an oven at 120°C for 24 hours. The resulting yellow liquid was washed several times with ethyl ether and then dried in a vacuum oven at 80°C for 24 hours as follows: ¹HNMR (DMSO-d₆, 500 MHz) δ: 0.51 (t,2H), 1.04–1.16 (m,9H), 1.82 (d,2H), 3.67–3.76 (m,6H), 3.87 (s,3H), 4.14 (t,2H), 7.77 (m,1H), 7.84 (m,1H), and 9.25 (s,1H).

2.1.2. Synthesis of Polysiloxane Grafted with Imidazolium Iodide Moieties (IL-SiO₂). An amount of TESPIm⁺I⁻ and tetraethoxysilane (TEOS) was mixed in ethanol. The molar ratios of TESPIm⁺I⁻/TEOS were 1/1, 2/1, respectively. 1 wt.% hydrochloric acid was then added under continuous stirring. The mixture was refluxed at 55°C for 6 hours and then dried via rotary evaporation to obtain yellow solid productions IL-SiO₂ (1/1), IL-SiO₂ (2/1), respectively (seeing Scheme 2).

2.2. Preparation of Gel Polymer Electrolytes. The porous polymer membrane composed of poly(vinylidene fluoride) (PVDF, SOLEF 1015) and IL-SiO₂ was synthesized by the phase inversion process. The dried polymer powders of PVDF and IL-SiO₂ were dissolved in N, N-dimethylformamide. The weight ratios of PVDF/(IL-SiO₂) polymer mixtures were 9/1, 8/2, 7/3, 6/4, 5/5, and 4/6, respectively. An amount of propanetriol as nonsolvent was

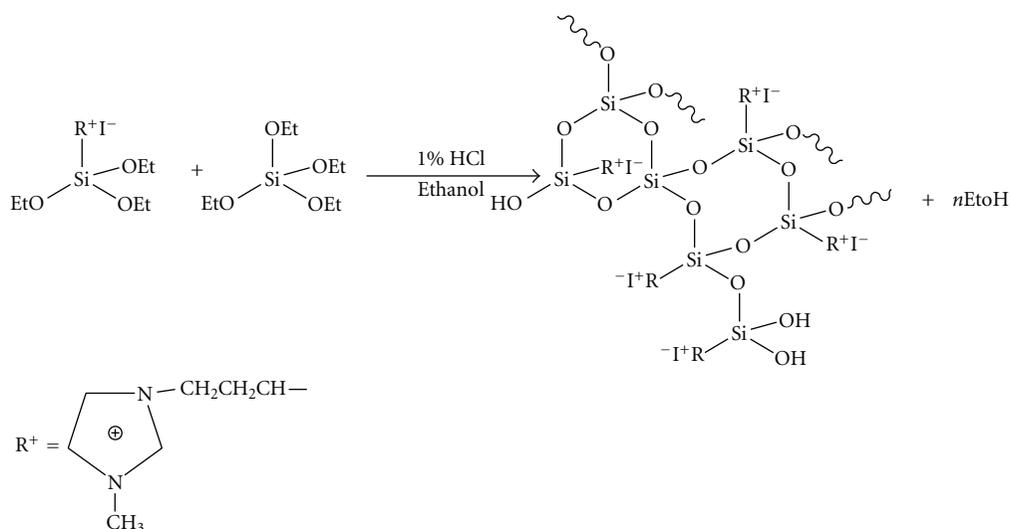
then added under continuous stirring at 60°C for 12 hours to form homogeneous hybrid. The resulting viscous mixture spread on a glass substrate was heated to 80°C for 24 hours to remove solvent and nonsolvent.

The formed films were immersed in ethanol to extract residual propanetriol. Finally, the dried polymer membranes were soaked in liquid electrolyte (0.5 mol/l NaI, 0.05 mol/l I₂, 0.1 mol/l 4-tert-butylpyridine) in the binary organic solvents mixture propylene carbonate and ethylene carbonate with 4:6 (w/w) for 12 hours to obtain the desired gel polymer electrolytes (GPEs). The thickness of the gel electrolyte was about 100 μm.

DSSCs Assembly. The TiO₂ film based on self-aligned highly ordered TiO₂ nanotube arrays was immersed in a 0.5 mMOL ethanol solution of *cis*-[(dcbH₂)₂Ru(SCN)₂] (N719; Solaronix) for 24 hours to absorb the dye adequately [17]. A quasi-solid-state dye-sensitized solar cell was assembled by sandwiching a slice of gel polymer electrolyte between a dye-sensitized TiO₂ electrode and a platinum counter electrode (purchased from DYESOL). The two electrodes were clipped together with clamps. The active area of the cell was 0.25 cm².

2.3. Measurements. ¹HNMR was recorded on a 500 MHz spectrometer (BRUKER DRX500) using DMSO-d₆ as solvent. The molecular weight of IL-SiO₂ was recorded on GPC. The morphology of IL-SiO₂ was analyzed by means of transmission electron microscopy (FEI Tecnai G2) with energy dispersive X-ray spectrometry (EDS). The X-ray diffraction (XRD) measurement was performed with a Bruker D8 diffractometer. The morphology of polymer membrane was characterized by scanning electron micrograph (Quanta200, FEI). The IR absorption spectra were taken using an attenuated total reflection Fourier transform infrared spectrometer (PerkinElmer1760) over the range from 600 to 4000 cm⁻¹. *n*-butanol absorption technique was used to measure the porosity of the polymer membranes [18]. The electrolyte uptake was calculated by $\text{Uptake} = (W_i - W_0)/W_0 \times 100\%$, where W_i and W_0 were the weight of the wet and dry membranes, respectively.

The measurement cell was made by sandwiching the GPE membrane between two Pt electrodes (Pt/electrolyte/Pt). The electrolyte resistance R_b was measured by AC impedance using CHI660 electrochemical workstation. The ionic conductivity of the GPE (σ) was calculated with the equation: $\sigma = d/R_b S$, where d is the thickness of electrolyte, S is the area of electrolyte.

SCHEME 2: Synthesis of IL-SiO₂.

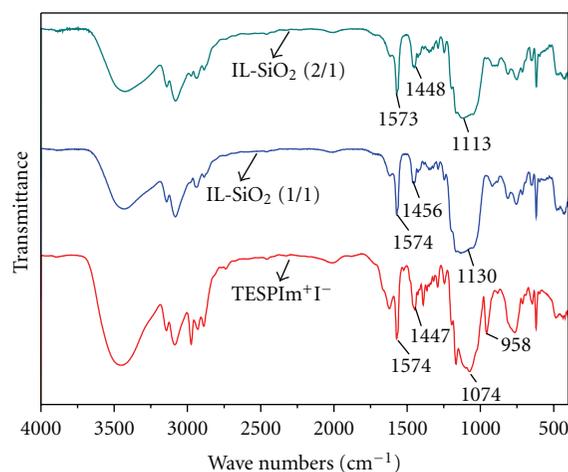
The steady-state voltammograms of GPE was performed to investigate the triiodide apparent diffusion coefficient (D) in the electrolyte. $D = I_{\text{lim}}d/2nFC$, where I_{lim} is limiting current density, n is the electron number per molecule, d is the thickness of gel electrolyte, F is the Faraday constant, and C is the bulk concentration of electroactive species [19].

Photocurrent-voltage characteristics of the DSSCs were obtained by a Keithley model 2400 digital source meter using an Oriel 91192 solar simulator equipped with AM 1.5 filter and intensity of 100 mW/cm². The fill factor (ff) and the conversion efficiency (η) of the cell are calculated by the following equations: $ff = P_{\text{max}}/I_{\text{sc}}V_{\text{oc}} = I_{\text{mp}}V_{\text{mp}}/I_{\text{sc}}V_{\text{oc}}$, $\eta = I_{\text{mp}}V_{\text{mp}}/P_{\text{in}} \times 100\%$, where I_{sc} is the short-circuit current density (mA cm⁻²), V_{oc} is the open-circuit voltage (V), and P_{in} is the incident light power. I_{mp} (mA cm⁻²) and V_{mp} (V) are the current density and voltage in the I - V curves, respectively, at the point of maximum power output.

3. Results and Discussion

3.1. Characterization of Polysiloxane Drafted with Imidazolium Iodide Moieties. Figure 1 shows FT-IR spectra of TESPI^{m+}I⁻ and two types of IL-SiO₂, IL-SiO₂ (1/1), and IL-SiO₂ (2/1). The disappearance of the vibration band at around 960 cm⁻¹ characteristic of SiOEt groups of the starting chemical and the presence of a strong vibration band from 1000 to 1200 cm⁻¹, attributable to Si-O-Si, in the FTIR spectrum of IL-SiO₂ confirms the formation of silica network [20]. Moreover, imidazolium iodide moieties contained in silica network is determined by the existence of sharp lines around 1570, 1467, corresponding to stretching vibration bands of imidazole ring. Also, the absorption peak at around 3400 cm⁻¹ indicates the presence of silanols.

It can be recognized that the relative intensity of the peaks corresponding to imidazole ring increases with increasing the molar ratios of TESPI^{m+}I⁻/TEOS, and at mean time

FIGURE 1: FT-IR spectra of TESPI^{m+}I⁻ and IL-SiO₂.

the relative intensity of the peaks corresponding to Si-O-Si decreases. It can be considered that the proportion of imidazolium iodide moieties in IL-SiO₂ (2/1) is higher than in IL-SiO₂ (1/1), but the inorganic contents in IL-SiO₂ (2/1) are lower than in IL-SiO₂ (1/1).

Both types of IL-SiO₂ can be dispersed to nanosized particles with no obvious agglomeration as clearly shown by the TEM image of Figure 2. It can be thought that the IL-SiO₂, made by the sol ± gel process by utilizing TEOS and TESPI^{m+}I⁻, is composed of covalently linked SiO₂ and imidazolium iodide moieties networks well mixed on the nanoscale. IL-SiO₂ (1/1) has narrow particle size distribution and a mean particle size of 200 nm (seeing Figure 2(a)). IL-SiO₂ (2/1) is evenly distributed about 10 nm in diameters, with very few big size particles about 100 nm in diameters (seeing Figure 2(b)). It is possible that in

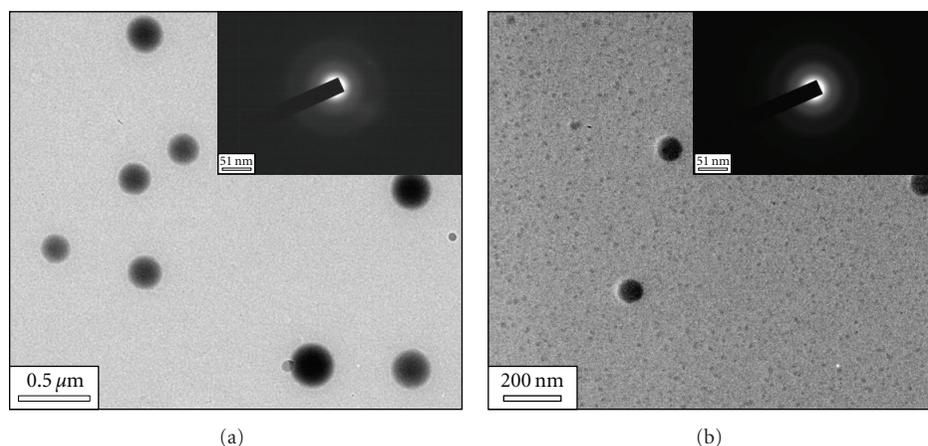


FIGURE 2: TEM images of IL-SiO₂. (a) IL-SiO₂ (1/1), (b) IL-SiO₂ (2/1).

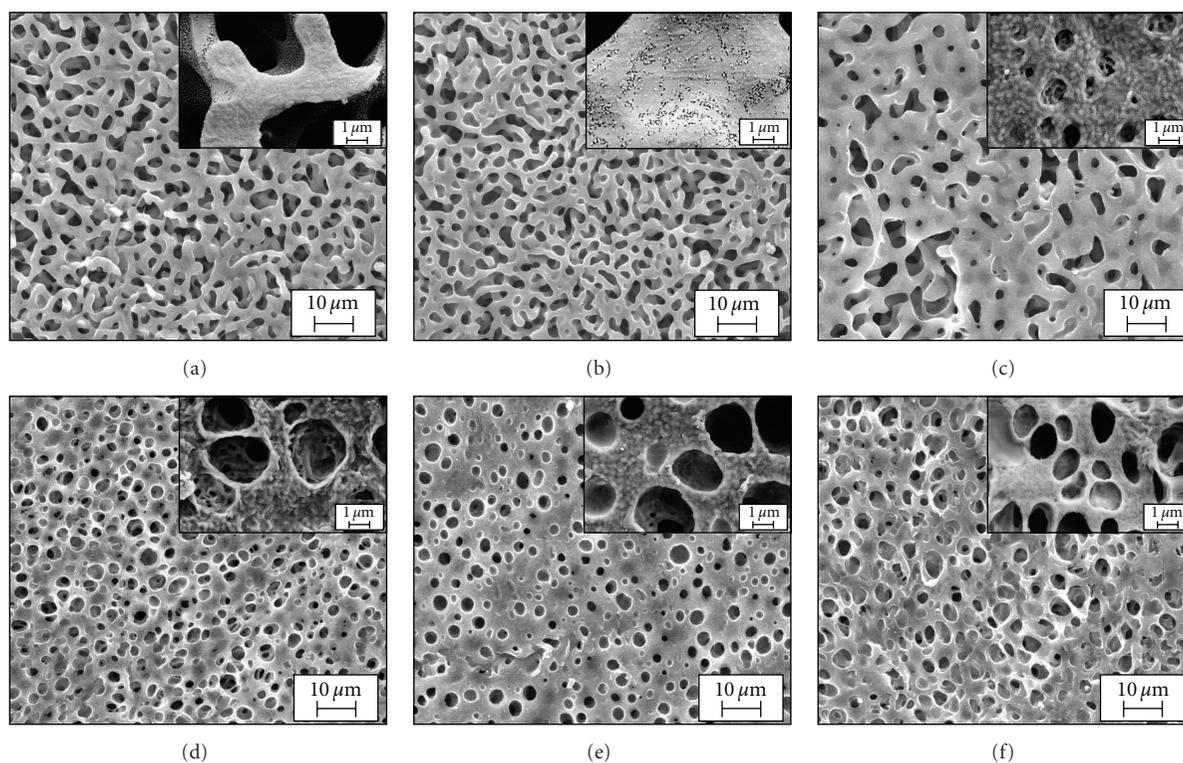


FIGURE 3: SEM images of polymer membranes PVDF/IL-SiO₂ (1/1). (a) the weight ratio of PVDF/IL-SiO₂ is 9/1. (b) the weight ratio of PVDF/IL-SiO₂ is 8/2. (c) the weight ratio of PVDF/IL-SiO₂ is 7/3. (d) the weight ratio of PVDF/IL-SiO₂ is 6/4. (e) the weight ratio of PVDF/IL-SiO₂ is 5/5. (f) the weight ratio of PVDF/IL-SiO₂ is 4/6.

addition to the TESPIm⁺I⁻ reacting with TEOS, self-condensation may also occur, leading to the formation of dimers, trimers, and higher oligomers of TESPIm⁺I⁻ or TEOS. And it is more likely that self-condensation occurs between TEOS for their higher activity than TESPIm⁺I⁻, so the size of particles increases with increasing the molar ratios of TESPIm⁺I⁻/TEOS. In addition, it can be drawn from electron diffraction analysis that both types of IL-SiO₂ are amorphous material.

The molecular weights (M_ws) and polydispersity index (PDI) of the IL-SiO₂ were determined using GPC (see Table 1). There is no great difference between two types of IL-SiO₂. The molecular weight of IL-SiO₂ (1/1) is a little bigger than that of IL-SiO₂ (2/1). It is believed that more imidazolium iodide moieties of TESPIm⁺I⁻ may impede the polycondensation of siloxane and, thus, hold back the growth of molecular chains.

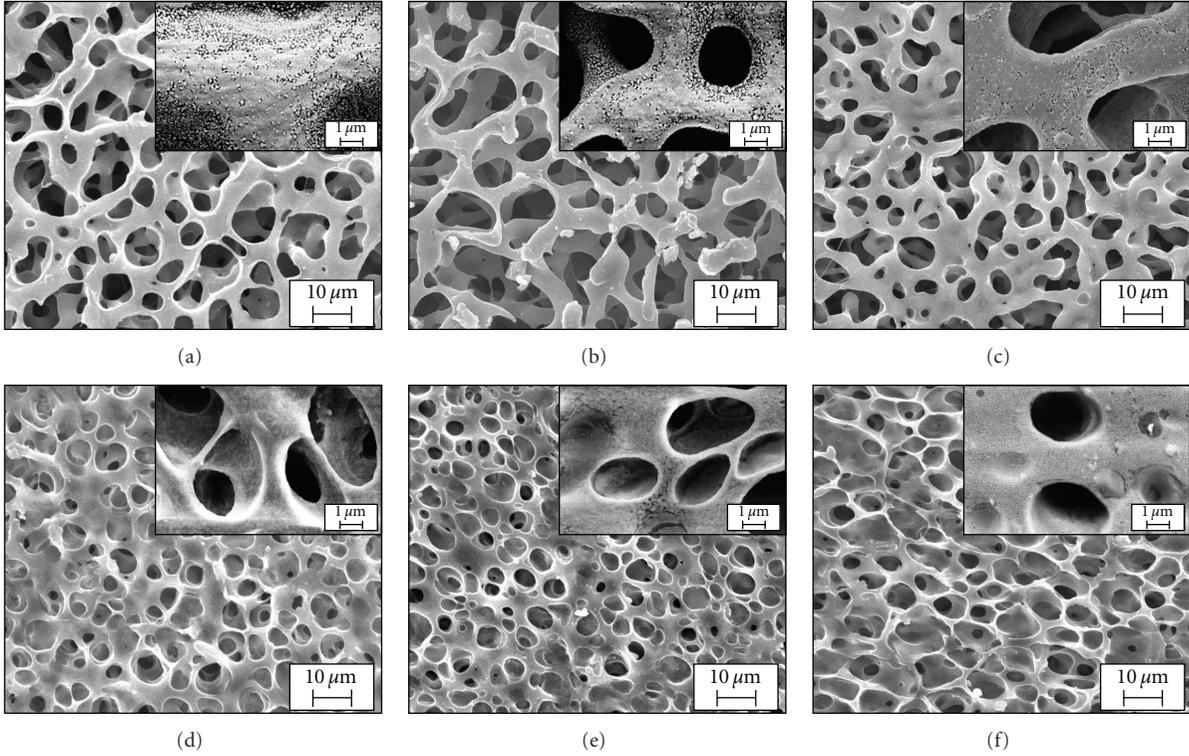


FIGURE 4: SEM images of polymer membranes PVDF/IL-SiO₂ (2/1). (a) the weight ratio of PVDF/IL-SiO₂ is 9/1. (b) the weight ratio of PVDF/IL-SiO₂ is 8/2. (c) the weight ratio of PVDF/IL-SiO₂ is 7/3. (d) the weight ratio of PVDF/IL-SiO₂ is 6/4. (e) the weight ratio of PVDF/IL-SiO₂ is 5/5. (f) the weight ratio of PVDF/IL-SiO₂ is 4/6.

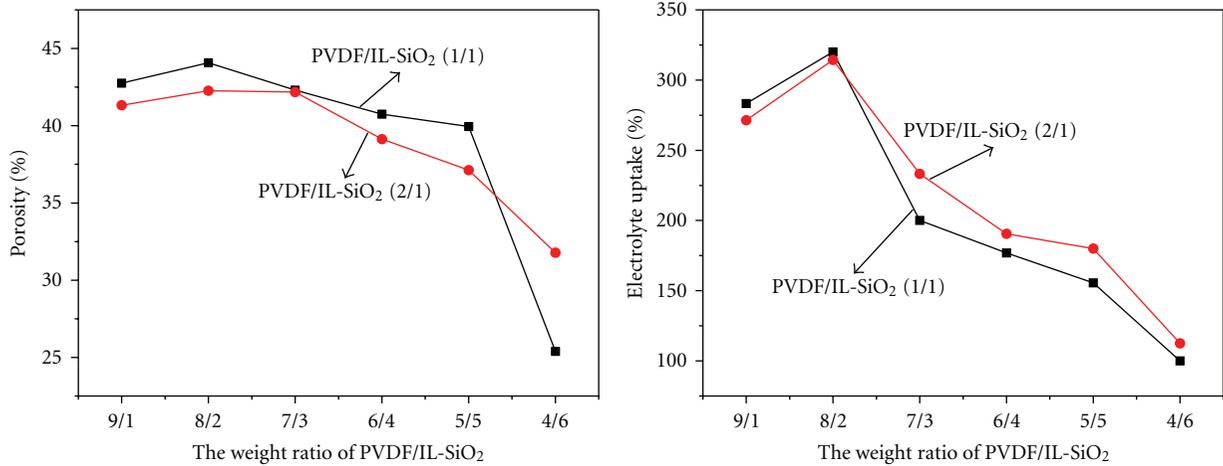


FIGURE 5: Porosity and electrolyte uptake of polymer membranes.

TABLE 1: The molecular weights of IL-SiO₂.

	The molar ratios of TESPIm ⁺ I ⁻ /TEOS	Mw (Daltons)	Polydispersity
IL-SiO ₂ (1/1)	1 : 1	8311	1.009253
IL-SiO ₂ (2/1)	2 : 1	8104	1.009567

3.2. Performances of Microporous Polymer Membranes. The surface of microporous polymer membranes with different

weight ratios of PVDF/IL-SiO₂ (1/1) and PVDF/IL-SiO₂ (2/1) was observed by SEM (seeing Figures 3 and 4).

The incorporation of IL-SiO₂ component into the microporous polymer matrix changed significantly the morphology. The membranes produced with low content IL-SiO₂ display regular porous structure (seeing Figures 3(a) and 3(b) and Figures 4(a) and 4(b)). The pore size of PVDF/IL-SiO₂ (2/1) membranes seems larger than that of PVDF/IL-SiO₂ (1/1). The interior of the membrane has a uniform porous structure as well as the exterior. This indicates that

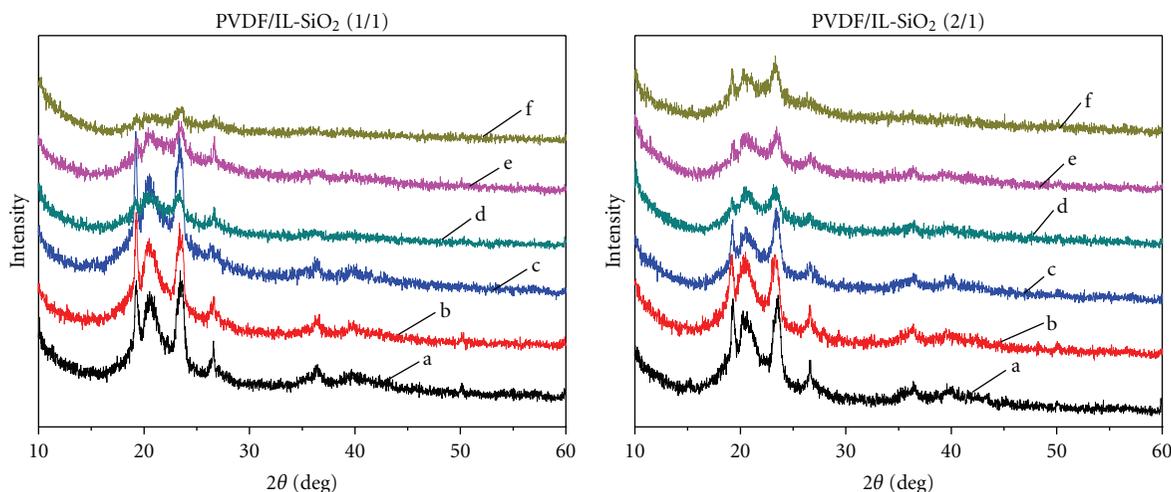


FIGURE 6: XRD patterns for PVDF/IL-SiO₂ polymer membranes. (a) PVDF/IL-SiO₂ (9 : 1 by weight). (b) PVDF/IL-SiO₂ (8 : 2 by weight). (c) PVDF/IL-SiO₂ (7 : 3 by weight). (d) PVDF/IL-SiO₂ (6 : 4 by weight). (e) PVDF/IL-SiO₂ (5 : 5 by weight). (f) PVDF/IL-SiO₂ (4 : 6 by weight).

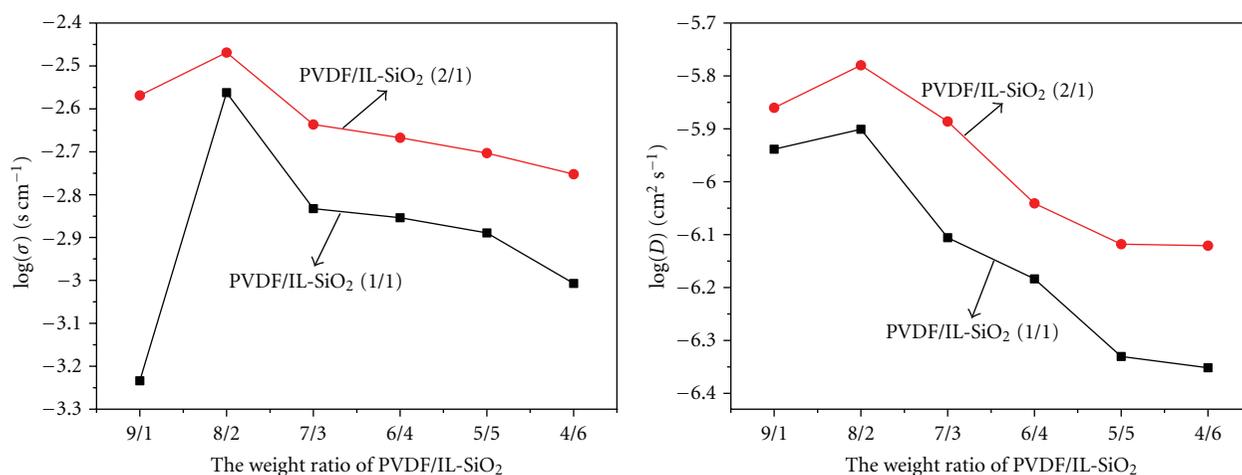


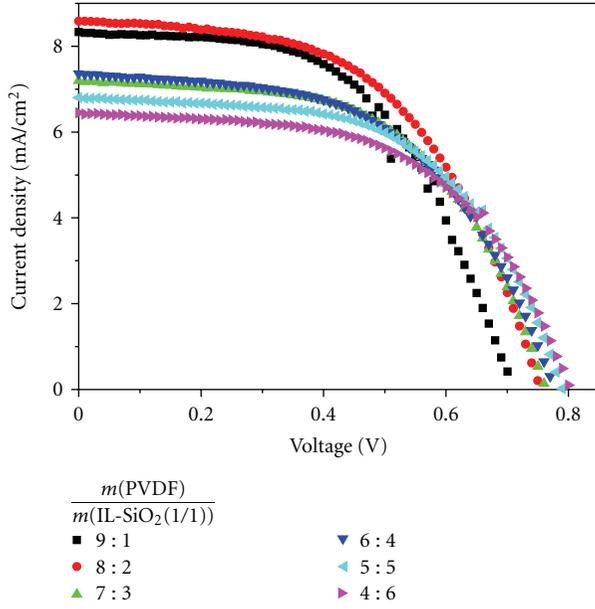
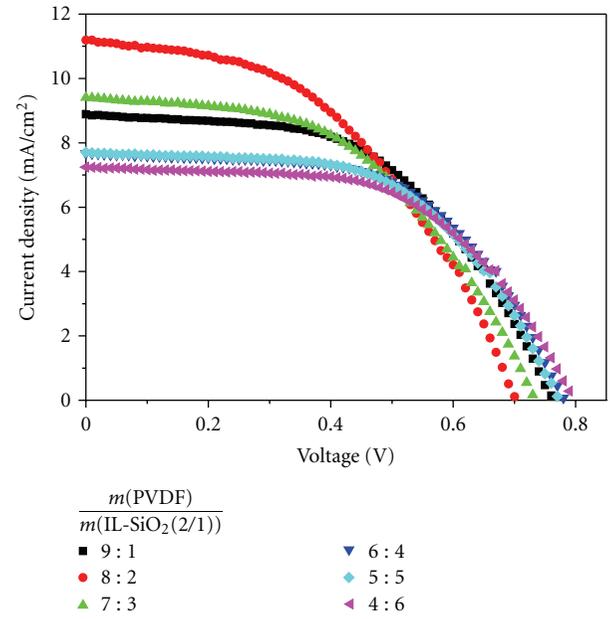
FIGURE 7: The ionic conductivity (σ) and the apparent diffusion coefficient of triiodide (D) of GPEs.

the cellular pores are all open with extensive pore-pore interconnections. But the size of the pores decreases with the increasing of the amount of IL-SiO₂. Meanwhile, the connectivity of porous structure becomes poor, appearing more closed pores (seeing Figures 3(c)–3(f) and Figures 4(c)–4(f)).

It also can be seen that IL-SiO₂ are dispersed well on the membrane surface when the weight ratio of PVDF/IL-SiO₂ is low. The imidazolium iodide moieties linked on SiO₂ are beneficial to prevent nanoparticle aggregation owing to the increase of distances between SiO₂. To PVDF/IL-SiO₂ (1/1) membrane, it is clear that residual silanol continue, to condensate forming more and bigger irregular particles when increasing the amount of IL-SiO₂ (seeing Figures 3(c)–3(f)). But no obvious big particles are observed in PVDF/IL-SiO₂ (2/1) membranes. We have reasons to think that the higher proportion of imidazolium iodide moieties in IL-SiO₂ (2/1) improved the particle dispersibility.

Figure 5 shows the porosity and electrolyte uptake of membranes with different polymer composition. The maximum of the porosity is observed when the weight ratio of PVDF/IL-SiO₂ polymer is 8/2. The tendency of the electrolyte uptake is similar to that of the porosity. It is notable that the porosity of PVDF/IL-SiO₂ (1/1) membranes is greater than PVDF/IL-SiO₂ (2/1) membranes, but the change law of electrolyte uptake is opposite. It can be thought that imidazolium iodide moieties grafted on polysiloxane are hopeful to efficient uptake of the liquid electrolyte.

The XRD characterization of pure IL-SiO₂ and the PVDF/IL-SiO₂ polymer membranes are shown in Figure 6. There is a decrease in the relative intensity of the apparent peaks corresponding to polymer membrane with increasing IL-SiO₂ concentrations. This fact indicates that the crystallinity of PVDF can be reduced with the addition of IL-SiO₂. The hydrogen bond formation of remained silanols and the hydrolyzed silane prevents the polymer

FIGURE 8: I-V curves of DSSCs with PVDF/IL-SiO₂ (1/1) GPEs.FIGURE 9: I-V curves of DSSCs with PVDF/IL-SiO₂ (2/1) GPEs.

chains to recrystallize [21]. Moreover, it can be seen that the relative intensity of the apparent peaks of PVDF/IL-SiO₂ (2/1) membranes is lower than that of PVDF/IL-SiO₂ (1/1) membranes. It means that the polysiloxane grafted with more imidazolium iodide moieties is propitious to reduce crystallinity of PVDF.

3.3. Ionic Conductivity and Triiodide Diffusion Coefficients of GPEs. EIS was used to characterize the electrochemical behavior of the gel polymer electrolyte. The ionic conductivity of the GPEs (σ) and the triiodide apparent diffusion coefficient (D) are summarized, respectively, in Figure 7.

IL-SiO₂ containing imidazolium iodide moieties show excellent compatibility with organic solvent or plasticizers, which is beneficial to form gel polymer electrolyte. Meanwhile, the crystallinity of the membrane is reduced with increasing IL-SiO₂ content as confirmed by XRD analysis. These favorable properties of IL-SiO₂ improve the conductivity of GPEs. But on the other hand, the porosity of the membrane decreases with increasing IL-SiO₂ content, leading to the drop of the conductivity of GPEs. As a result, the gel polymer electrolyte shows the highest σ and D when the weight ratio of PVDF/IL-SiO₂ polymer is 8/2 and then decreased.

The greatest value σ and D obtained is 3.40×10^{-3} and 1.66×10^{-6} of PVDF/IL-SiO₂ (2/1) system. Increasing the proportion of imidazolium iodide moieties in polysiloxane effectively improves the ionic conductivity and triiodide diffusion coefficients of GPEs for lower crystallinity and higher electrolyte uptake.

3.4. Photovoltaic Performance. The photocurrent performances for dye-sensitized solar cell with different electrolytes (A to F) were tested. The gel polymer electrolyte used in cell

TABLE 2: Photovoltaic performances of DSSCs with PVDF/IL-SiO₂ (1/1) GPEs.

Cell	V_{oc}	$I_{sc}/\text{mA cm}^{-2}$	ff	$\eta/\%$
A	0.708	8.324	0.547	3.224
B	0.754	8.584	0.535	3.462
C	0.760	7.196	0.563	3.082
D	0.770	7.360	0.540	3.064
E	0.790	6.800	0.568	3.054
F	0.799	6.448	0.559	2.884

TABLE 3: Photovoltaic performances of DSSCs with PVDF/IL-SiO₂ (2/1) GPEs.

Cell	V_{oc}	$I_{sc}/\text{mA cm}^{-2}$	ff	$\eta/\%$
A	0.763	8.888	0.527	3.576
B	0.702	11.192	0.459	3.611
C	0.733	9.408	0.497	3.429
D	0.782	7.676	0.572	3.432
E	0.772	7.708	0.564	3.359
F	0.796	7.240	0.567	2.272

A is PVDF/IL-SiO₂ (9:1 m/m); in cell B is PVDF/IL-SiO₂ (8:2 m/m); in cell C is PVDF/IL-SiO₂ (7:3 m/m); in cell D is PVDF/IL-SiO₂ (6:4 m/m); in cell E is PVDF/IL-SiO₂ (5:5 m/m); in cell F is PVDF/IL-SiO₂ (4:6 m/m). The I-V curves of DSSCs with PVDF/IL-SiO₂ (1/1) GPEs and DSSCs with PVDF/IL-SiO₂ (2/1) GPEs are shown in Figures 8 and 9, respectively. And cell parameters corresponding to these DSSCs are summarized in Tables 2 and 3, respectively.

The addition of IL-SiO₂ (2/1) brought a significant improvement of the short-circuit current (I_{sc}) and the cell efficiency (η). It could be attributed to better nanoparticle

dispersibility in polymer network of PVDF/IL-SiO₂ (2/1), which promotes the movement of free ions in a regular direction. At the microscopic level, it maintains a “liquid-” like structure, which is important for sufficient conductivity [22]. While the high density of network formed by Si–O–Si in PVDF/IL-SiO₂ (2/1) might hinder the charge transfer thus reduce the cell performance.

The variable trend of I_{sc} and η can also be recognized from the variation of the ionic conductivity of the GPEs (σ) and the triiodide apparent diffusion coefficient (D) as indicated in Figure 7. The diffusion of triiodide (D) plays a major role in DSSC performance. The faster transportation speed of the triiodide leads to the faster reduction of I⁻, and the faster reduction of excited dye molecule [23]. PVDF/IL-SiO₂ (2/1) GPEs showed higher σ and D than PVDF/IL-SiO₂ (1/1) GPEs. As a result, the cell employing GPE of PVDF/IL-SiO₂ (2/1) with the weight of 8/2 showed preferable photovoltaic performances. However, due to the poor conductive property when too much IL-SiO₂ added, the cells of both systems showed lower short-circuit current and lower energy conversion efficiency.

4. Conclusions

We have synthesized two types of polysiloxane grafted with different ration imidazolium iodide moieties, IL-SiO₂ (1/1) and IL-SiO₂ (2/1), through the sol-gel method. A gel polymer electrolyte based on PVDF/IL-SiO₂ was prepared by soaking a porous membrane in an organic electrolyte solution containing the I⁻/I₃⁻ redox couple. IL-SiO₂ (2/1) with higher proportion of imidazolium iodide moieties improved the compatibility with liquid electrolyte and polymer matrix more effectively for its ionic liquid characteristics. The greatest value σ and D obtained is $3.40 \times 10^{-3} \text{ S cm}^{-1}$ and $1.66 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ of PVDF/IL-SiO₂ (2/1) system. The electrolytes prepared using this new inorganic/organic polymer composite improved cell performance by increasing I_{sc} presumably through creating specific pathways for ion transportation and better ion conductive performance. A dye-sensitized solar cell employing GPE of PVDF/IL-SiO₂ (2/1) (8:2 m/m) yielded an open-circuit voltage of 0.702 V, short-circuit current of 11.192 mA cm⁻², and the conversion efficiency of 3.611% at 1 sun illumination. The optimization of many parameters for the electrode preparation and the cell assembling is under study and further improvement of the photovoltaic performance is expected in the near future.

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