

Preparation and Characterization of a Microporous Polymer Electrolyte Based on Poly(vinylidene fluoride)/Ionic-Liquid-Functionalized SiO₂ for Dye-Sensitized Solar Cells

Yang Yan, Tao Jie, Jin Xin, Qin Qi

College of Material Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, People's Republic of China

Received 12 March 2010; accepted 2 November 2010

DOI 10.1002/app.33746

Published online 3 March 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A new type of ionic-liquid-functionalized SiO₂ (IL-SiO₂) was synthesized to develop a microporous polymer electrolyte for quasi-solid-state dye-sensitized solar cells. The samples were characterized by ¹H-NMR, Fourier transform infrared spectroscopy, transmission electron microscopy, scanning electron microscopy, and X-ray diffraction. Moreover, the ionic conductivity of the electrolytes was measured by an electrochemical workstation. Nanostructured silica containing imidazolium iodide showed excellent compatibility with the organic solvent.

The incorporation of the IL-SiO₂ component into the polymer matrix improved the electrochemical behavior of the gel polymer electrolyte. A dye-sensitized solar cell with a gel polymer electrolyte yielded an open-circuit voltage of 0.662 V, a short-circuit current of 13.40 mA/cm², and a conversion efficiency of 4.01% at 1 sun illumination. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1566–1573, 2011

Key words: electrochemistry; membranes; nanocomposites; polysiloxanes

INTRODUCTION

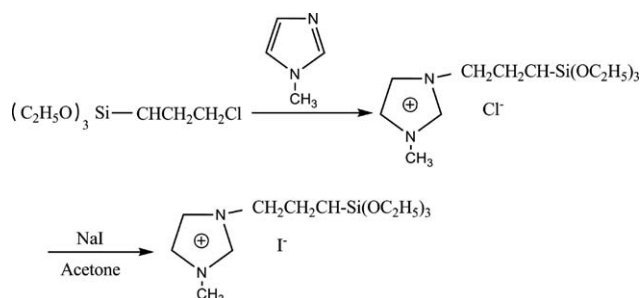
Because of the high conversion efficiency of solar energy to electric power and its low production cost, dye-sensitized solar cells (DSSCs) have attracted widespread scientific and technological interest and have evolved as potential alternatives to traditional photovoltaic devices in the past decade.¹ However, one of the main problems is that liquid electrolytes limit device stability because of their easy evaporation and leakage. Therefore, organic and inorganic hole-transport materials,^{2,3} ionic liquids,^{4–6} and polymeric electrolytes^{7–9} have been considered as solid or quasi-solid-state substitutes for liquid electrolytes.

Many studies have also focused attention on inorganic/organic polymer composite electrolytes. The nanoparticle/polymer composite structure was designed because the ordering of the electrolyte structure was beneficial for electron hopping (exchange reaction).^{10,11} An efficiency close to 7% was achieved for modified quasi-solid electrolytes with poly(vinylidene fluoride-co-hexafluoropropylene) and silica nanoparticles to solidify solvent-based electrolytes.¹² Lianos et al.¹³ used a nanocomposite silica-based gel with an

organic subphase containing propylene carbonate, 1-methyl-3-propylimidazolium iodide, and Triton as a surfactant. When applied as an electrolyte in DSSCs, it gave a maximum efficiency of 5.4%. The same group achieved an efficiency of 5–6% with a nanocomposite organic–inorganic sol–gel electrolyte; this incorporated a hydrolysable alkoxysilane derivative.¹⁴ Cerneaux et al.¹⁵ prepared a series of new quaternary ammonium iodide silica based compounds. These hybrid organic–inorganic materials were used as iodide sources in the preparation of electrolyte solutions for DSSCs, and the best efficiency of 8.6% was obtained. Mizumo et al.¹⁶ first reported composite materials based on polymerized ionic liquid and an inorganic matrix. The polymerization of ionic liquids was carried out successfully in parallel with the sol–gel reactions of tetramethoxysilane (TMOS) and alkoxyboranes. It was confirmed that to add functions to the composites under mild conditions without a loss in the mechanical strength or the inherent properties of the polymerized ionic liquids was a valuable method.

The nanoparticles can prevent the volatility and leakage of the electrolyte and improve the mechanical strength of the cell as well. However, these nanoparticles are apt to aggregate to become larger particles, which easily settle onto the surface of TiO₂ photoanodes and retard ion transportation on the electrode surface. One of the effective ways of improving the dispersion of nanoparticles in a

Correspondence to: T. Jie (taojie@nuaa.edu.cn).



Scheme 1 Synthesis of 1-propyl-3-triethoxy silica-3-methylimidazolium iodide (TESPIm⁺I⁻).

polymer matrix is the use of particle surface modification. Room-temperature ionic liquids are attractive candidates for the replacement of volatile organic solvents because of their low volatility, high ionic conductivity, and good solubility for organics and inorganics.^{17,18} Ionic-liquid-functionalized SiO₂ (IL-SiO₂) has been reported as a high-performance liquid chromatography stationary phase¹⁹ and recyclable catalyst.²⁰ It is expected that this inorganic/organic polymer applied as an electrolyte in DSSC can not only enhance the stability of the electrolytes and the lifetime of the DSSC but also modify the compatibility with organic solvents or plasticizers because of its ionic liquid characteristics.

It is known that poly(vinylidene fluoride) (PVDF) is photochemically stable, even in the presence of TiO₂ and Pt nanoparticles. PVDF used as a hybrid electrolyte can effectively decrease back-electron transfer.^{21,22} Herein, we prepared a microporous gel electrolyte based on PVDF and IL-SiO₂ by soaking a porous membrane in an organic electrolyte solution containing an I⁻/I₃⁻ redox couple. In this study, nanostructured silica containing imidazolium iodide moieties was designed with a two-step route. First, imidazolium iodide containing a triethoxy-silane group (TESPIm⁺I⁻) was prepared. Then, functional silica nanoparticles were synthesized by the sol-gel process with tetraethoxysilane (TEOS) and TESPIm⁺I⁻. The properties of the gel electrolyte and the corresponding quasi-solid-state DSSCs were carefully studied with various measurement methods to determine the rule between the performance and the addition of IL-SiO₂.

EXPERIMENTAL

Silica nanoparticle functionalization

Synthesis of TESPIm⁺I⁻

The imidazolium iodide type ionic liquid, namely, TESPIm⁺I⁻, was synthesized with Teflon-lined, stainless autoclaves under solvent-free conditions (Scheme 1). It was an improved and environmentally friendly preparation. The mixture of 1-methylimidazolium (75.0 mmol) and 3-chloropropyltriethoxy-

silane (80.0 mmol) was placed in a 50-mL, Teflon-lined, stainless steel autoclave and was then heated in an oven at 120°C for 24 h. The resulting yellow liquid was washed several times with ethyl ether and then dried in a vacuum oven at 80°C for 24 h.

¹H-NMR (hexadeuterated dimethyl sulfoxide, 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), 9.25 (s, 1H).

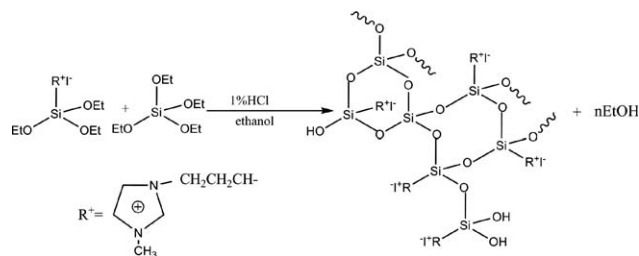
Synthesis of the nanostructured silica containing imidazolium iodide moieties (IL-SiO₂)

The functional silica nanoparticles were synthesized by the sol-gel process with TEOS and TESPIm⁺I⁻ (Scheme 2). Thirty millimoles of TESPIm⁺I⁻, 60 mmol of TEOS, and 5.75 mL of hydrochloric acid (1 wt %) were mixed with 50 mL of ethanol. The mixture was refluxed at 55°C for 6 h and then dried via rotary evaporation to obtain a yellow solid (IL-SiO₂).

Preparation of the polymer electrolyte

The dry porous polymer membrane composed of 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 the PVDF/(IL-SiO₂) polymer mixtures were 9/1, 8/2, 7/3, 6/4, 5/5, and 6/4. An amount of propanetriol as a nonsolvent was then added under continuous stirring at 60°C for 12 h to form a homogeneous hybrid. The resulting viscous mixture spread on a glass substrate was heated to 80°C for 24 h to remove the 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-butyl pyridine in the binary organic solvent mixture of propylene carbonate and ethylene carbonate with a ratio of 4:6 (w/w)) for 12 h to obtain the desired gel polymer electrolytes (GPEs).



Scheme 2 Synthesis of the nanostructured silica containing imidazolium iodide moieties (IL-SiO₂).

TABLE I
Molecular Weights of IL-SiO₂

	M_n (Da)	M_w (Da)	PDI
IL-SiO ₂	7677	7743	1.009

DSSC assembly

The preparation of the dye-sensitized TiO₂ film was similar to the previous report.²³ A quasi-solid-state DSSC was assembled by sandwiching a slice of GPE between a dye-sensitized TiO₂ electrode and a Pt counter electrode (purchased from DYESOL, Queanbeyan NSW, Australia). The two electrodes were clipped together with clamps. The active area of the cell was 0.25 cm².

Measurements

¹H-NMR was recorded on a 500-MHz spectrometer (Bruker DRX500, Bruker BioSpin GmbH, Rheinstetten, Germany) with hexadeuterated dimethyl sulfoxide as the solvent.

The molecular weight of IL-SiO₂ (see Table I) was estimated with a Waters 1515 gel permeation chromatography system, Waters Corporation, Milford, USA equipped with a Waters 2414 UV-vis detector and HP3-HP5 calibration columns with dimethylformamide as an eluent at a flow rate of 1 mL/min.

Transmission electron microscopy (TEM) images and selected area electron diffraction pictures were recorded on a FEI Tecnai G2 transmission electron microscope, FEI Europe, Eindhoven, the Netherlands at an accelerating voltage of 300 kV. Samples were dispersed in ethanol (high-performance liquid chromatography grade) with an ultrasonic cleaner for 5 min and fixed on a carbon-coated copper grid.

The X-ray diffraction (XRD) measurement was performed on a Bruker D8 diffractometer with graphite monochromatized Cu K α radiation (λ = 0.15418 nm) and a nickel filter.

The morphology of the polymer membrane was characterized by field emission scanning electron microscopy (SEM; LEO-1530VP, Carl Zeiss, ROSSDORF, GERMANY) with an accelerating voltage of 5.0 kV *in vacuo* after it was sputtered with gold at 10 mA for 10 min.

The IR absorption spectra were taken with an attenuated total reflection Fourier transform infrared (FTIR) spectrometer (PerkinElmer1760, PerkinElmer Corporate, Waltham, Massachusetts, USA) over the range from 600 to 4000 cm⁻¹ at a maximum resolution of 1 cm⁻¹.

We made the measurement cell by sandwiching the GPE membrane between two Pt electrodes (Pt/electrolyte/Pt). We measured the ionic conductivity of GPE (σ) by alternating-current impedance using a

CHI660 electrochemical workstation, Shanghai Chenghua Instrument Ltd, Shanghai, China in the frequency range from 10⁻² to 10⁵ Hz with amplitude of 5 mV. Steady-state voltammograms of GPE were obtained to investigate the apparent diffusion coefficient of triiodide (D) in the electrolyte. The system was polarized from 0 to 1 V at a rate of 10 mV/s.

The photocurrent-voltage characteristics of the DSSCs were obtained by a Keithley model 2400 digital source meter with an Oriel 91192 solar simulator Newport Corporation Stratford, CT, USA equipped with an AM 1.5 filter and an intensity of 100 mW/cm².

RESULTS AND DISCUSSION

Characterization of the nanostructured silica containing imidazolium iodide moieties

FTIR spectroscopy

Figure 1 shows the FTIR spectra of TESPIIm⁺I⁻ and IL-SiO₂. The disappearance of the vibration band 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 confirmed the formation of the silica network.²⁴ Moreover, the presence of imidazolium iodide moieties contained in the silica network were determined by the existence of sharp lines around 1572 and 1447 cm⁻¹, which corresponded to stretching vibration bands of the imidazole ring. Also, the absorption peak around 3400 cm⁻¹ indicated the presence of silanols.

TEM analysis

As clearly shown by the TEM image of Figure 2, the IL-SiO₂ nanoparticles had diameters from 10 to 600 nm and good dispersion with few aggregates.

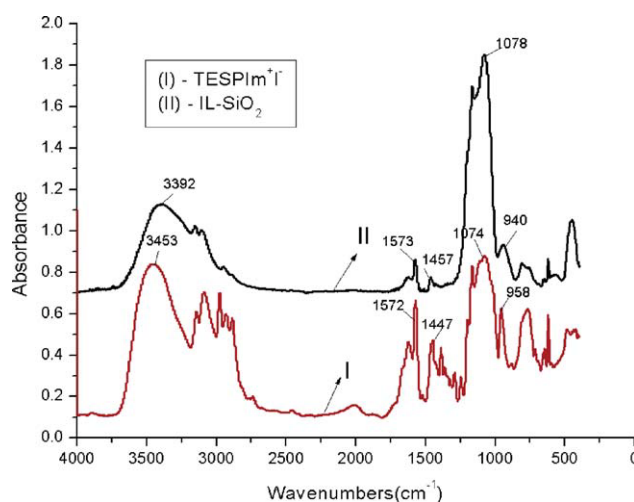


Figure 1 FTIR spectra of TESPIIm⁺I⁻ and IL-SiO₂. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

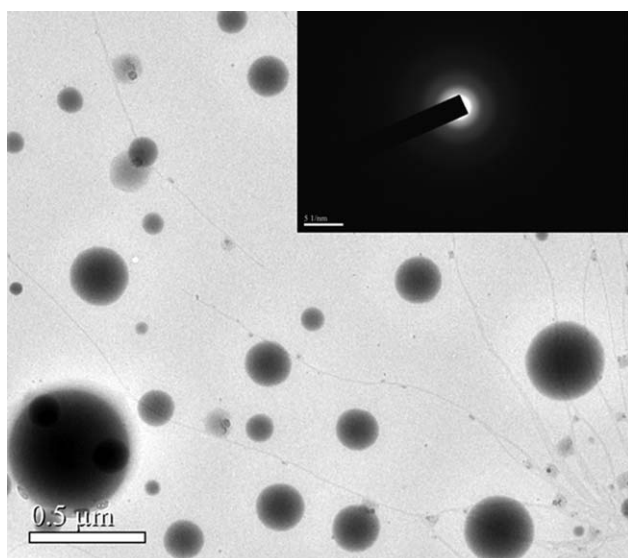


Figure 2 TEM image of IL-SiO₂.

Figure 3 shows the size distribution of the IL-SiO₂ nanoparticles. The nanoparticle size of about 50 nm accounted for 56.62% of the particles. It is possible that in addition to the TESPI⁺Im⁺I⁻ reacting with TEOS, self-condensation may also have occurred, leading to the formation of dimers, trimers, and higher oligomers of TESPI⁺Im⁺I⁻ or TEOS. It was more likely that self-condensation occurred between TEOS for their higher activity than TESPI⁺Im⁺I⁻, so the particle size distribution was relatively wide. In addition, we concluded from electron diffraction analysis that IL-SiO₂ was an amorphous material because its pattern consisted of fuzzy circles of light on the fluorescent screen.

Molecular weight measurement

The molecular weights [number-average molecular weight (M_n) and weight-average molecular weight (M_w)] and polydispersity index (PDI) of the IL-SiO₂ were determined with gel permeation chromatography (see Table I). It is possible that in addition to the TESPI⁺Im⁺I⁻ reacting with TEOS, self-condensation may have also occurred, leading to the formation of dimers, trimers, and higher oligomers of TESPI⁺Im⁺I⁻ or TEOS. The final product, after sol-gel transformation, was composed of covalently linked SiO₂ and imidazolium iodide moiety networks, well mixed on the nanoscale.

Performances of the microporous polymer membranes

Morphology

The surface of the microporous polymer membranes with different weight ratios of PVDF/IL-SiO₂ was observed by SEM (see Fig. 4). The incorporation of the

IL-SiO₂ component into the microporous polymer matrix significantly changed the morphology. The membranes produced with a low content of IL-SiO₂ displayed regular porous structures [see Fig. 4(a–c)]. IL-SiO₂ was dispersed well on the membrane surface [see Fig. 4(A–C)]. Because of the imidazolium iodide moieties contained in IL-SiO₂, which showed excellent compatibility with organic solvents, IL-SiO₂ dissolved exactly and did not just disperse in dimethylformamide during the polymer membrane preparation process by the phase-inversion method. This was helpful for the nanoparticles to disperse well in the polymer network. Simultaneously, the imidazolium iodide moieties linked on SiO₂ were beneficial for preventing nanoparticle aggregation because of the increase in distances between SiO₂. However, the size of the pores decreased with the increase in the amount of IL-SiO₂ because the nanoparticles started to agglomerate at higher addition amounts. Residual silanol continued to condensate, forming more and bigger irregular particles [see Fig. 4(D,e,f)].

Porosity and electrolyte uptake

According to Saito et al.,²⁵ the porosity, one of the important parameters of porous polymer membranes, can dominate the conduction properties of the carriers. Thus, the *n*-butanol absorption technique was used to measure the porosity of the polymer membranes.²⁶ The electrolyte uptake was calculated as follows:

$$\text{Uptake} = (W_i - W_0)/W_0 \times 100\%$$

where W_i and W_0 are the weights of the wet and dry membranes, respectively. Figure 5 shows the porosity and electrolyte uptake of membranes with

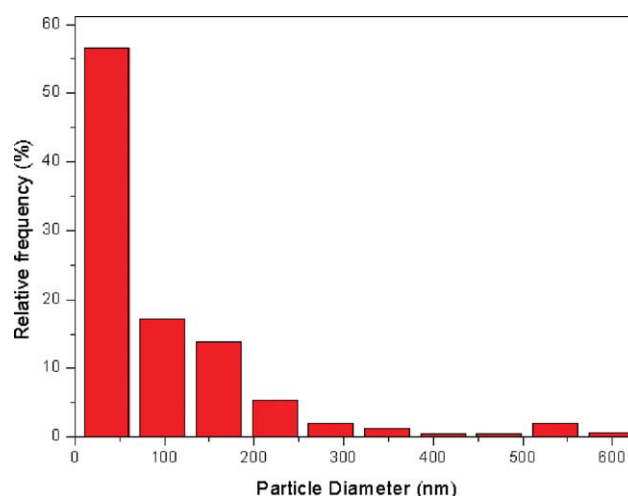


Figure 3 Size distribution of IL-SiO₂. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

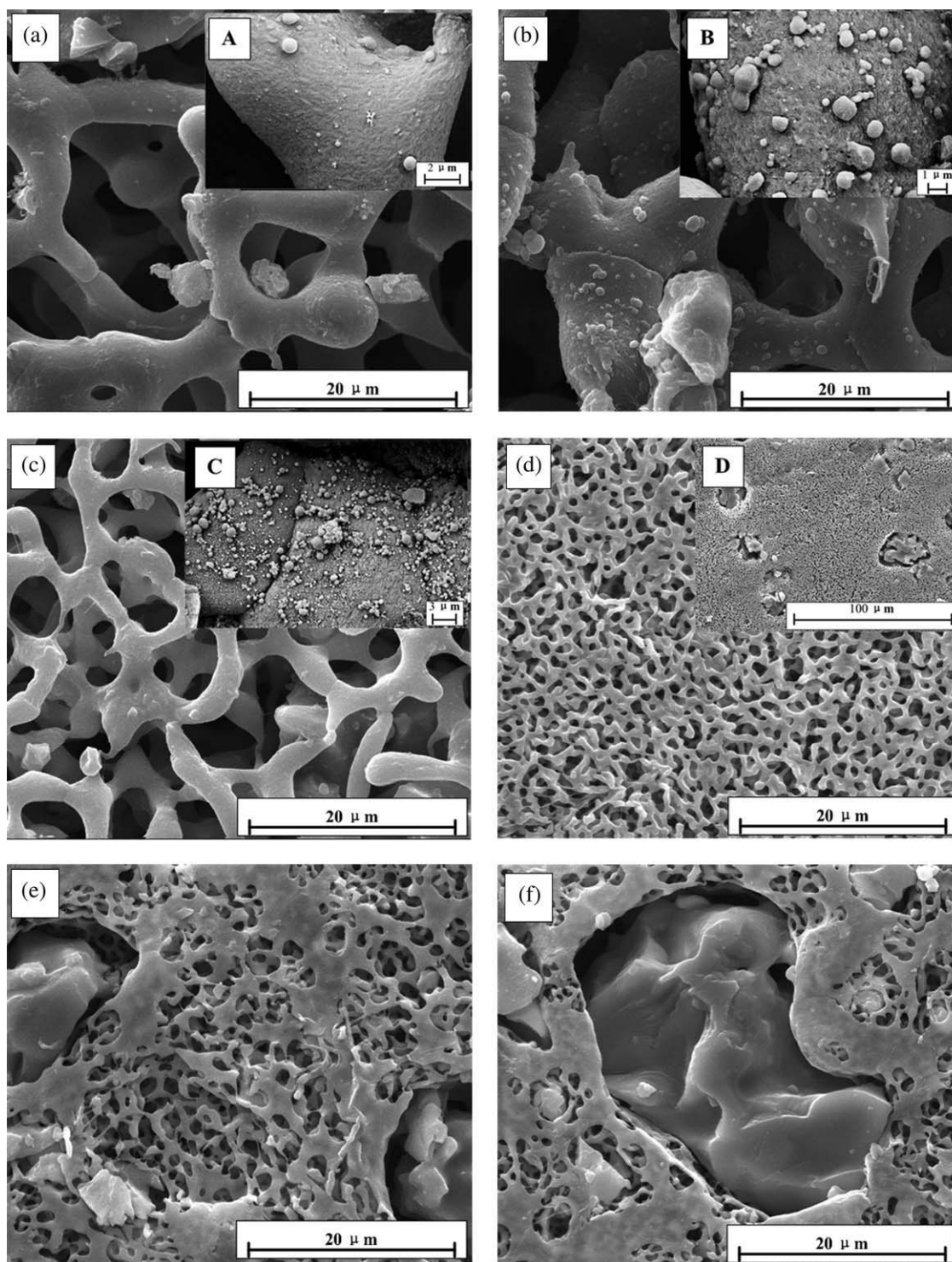


Figure 4 SEM images of the dry polymer membranes: (a) PVDF/IL-SiO₂ (9 : 1 by weight), (b) PVDF/IL-SiO₂ (8 : 2 by weight), (c) PVDF/IL-SiO₂ (7 : 3 by weight), (d) PVDF/IL-SiO₂ (6 : 4 by weight), (e) PVDF/IL-SiO₂ (5 : 5 by weight), and (f) PVDF/IL-SiO₂ (4 : 6 by weight).

different polymer compositions. The maximum porosity is observed when the weight ratio of the PVDF/IL-SiO₂ polymer was 8/2. The tendency of the electrolyte uptake was similar to that of the porosity. GPEs with 20 wt % IL-SiO₂ and 80 wt % PVDF had the maximum electrolyte uptake of

282.35%. The IL-SiO₂ nanoparticles were partially aggregated to form a microdomain phase-separated from the PVDF phase. The presence of microspores in the polymer network led to the efficient uptake of the liquid electrolyte when it was soaked in an electrolyte solution. However, too much IL-SiO₂ tended

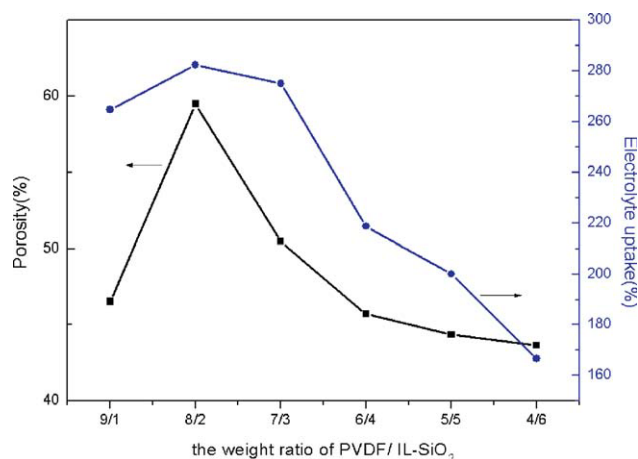


Figure 5 Porosity and electrolyte uptake of the polymer membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to destroy the regular porous structure and result in less absorption of the liquid electrolyte. As reported by Kim et al.²⁷ and Jeon et al.²⁸ At low nanoparticle loadings, there was good dispersion of nanoparticles in the porous membranes. At higher nanoparticle loadings, however, the nanoparticles started to agglomerate. This accounted for the decrease in the uptake of viscous electrolyte in the porous membranes.

XRD characterization

The XRD characterization of pure IL-SiO₂ and the PVDF/IL-SiO₂ polymer membranes is shown in Figure 6. No crystalline peak corresponding to IL-SiO₂ [see Fig. 6(a)] was observed; this was consistent with the results of the electron diffraction analysis. There was a decrease in the relative intensity of the apparent peaks corresponding to the polymer membrane with increasing IL-SiO₂ concentration [see Fig. 6(b–g)]. This fact indicated that the crystallinity of PVDF was reduced with the addition of IL-SiO₂.²⁹ The hydrogen-bond formation of the remaining silanols and the hydrolyzed silane prevented the polymer chains from recrystallizing.³⁰ The addition of IL-SiO₂ nanofillers may have favored the formation of complexes with the polymer and, in turn, may have acted as a crosslinking center for the polymer by reducing the tension of the polymer for self-organization and promoting stiffness.³¹

σ and D values of GPEs

Electrochemical Impedance Spectra (EIS) was used to characterize the electrochemical behavior of the GPE. σ was calculated as follows:

$$\sigma = d/R_b S$$

where d is the thickness of the electrolyte and S is the area of the electrolyte. The electrolyte resistance (R_b)

was measured with a CHI660 electrochemical workstation. The apparent D 's were calculated as follows:

$$D = I_{\text{lim}} d / 2nFC$$

where I_{lim} is the limiting current density, n is the electron number per molecule, d is the thickness of the gel electrolyte, F is the Faraday constant, and C is the bulk concentration of electroactive species.³² The σ and D values are summarized in Table II.

IL-SiO₂ containing imidazolium iodide moieties showed excellent compatibility with organic solvents and plasticizers; this was beneficial for the formation of GPEs. On the other hand, IL-SiO₂ was also very compatible with the PVDF polymer matrices at low addition amounts. The crystallinity of the membrane decreased with increasing IL-SiO₂ content, as confirmed by XRD analysis. These favorable properties of IL-SiO₂ made it easy and convenient to form polymer gel electrolytes with polymer matrices. However, meanwhile, the porosity of the membrane decreased with increasing IL-SiO₂ content; this led to a drop in the conductivity of the GPEs. As a result, the GPEs showed the highest σ and D when the weight ratio of the PVDF/IL-SiO₂ polymer was 8/2 and then decreased. The greatest values of σ and D obtained were 2.79×10^{-3} and 2.54×10^{-6} , respectively.

Photovoltaic performance

The photocurrent performances for DSSCs with different electrolytes (A to F) were tested. The fill

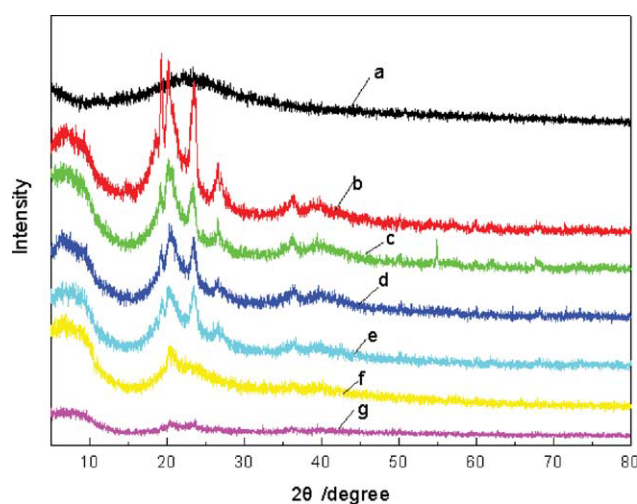


Figure 6 XRD patterns for the pure IL-SiO₂ and PVDF/IL-SiO₂ polymer membranes: (a) pure IL-SiO₂, (b) PVDF/IL-SiO₂ (9 : 1 by weight), (c) PVDF/IL-SiO₂ (8 : 2 by weight), (d) PVDF/IL-SiO₂ (7 : 3 by weight), (e) PVDF/IL-SiO₂ (6 : 4 by weight), (f) PVDF/IL-SiO₂ (5 : 5 by weight), and (g) PVDF/IL-SiO₂ (4 : 6 by weight). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
 σ and Apparent D Values of GEPs

mPVDF/mLIL-SiO ₂	9/1	8/2	7/3	6/4	5/5	4/6
σ (S/cm)	1.59×10^{-3}	2.79×10^{-3}	2.29×10^{-3}	1.68×10^{-3}	1.03×10^{-3}	8.93×10^{-4}
D (cm ² /s)	8.73×10^{-7}	2.54×10^{-6}	2.10×10^{-6}	1.80×10^{-6}	8.17×10^{-7}	5.76×10^{-7}

factor (ff) and the conversion efficiency (η) of the cell were calculated by the following equations:

$$ff = P_{\max}/I_{sc}V_{oc} = I_{mp}V_{mp}/I_{sc}V_{oc}$$

$$\eta = I_{mp}V_{mp}/P_{in} \times 100\%$$

where I_{sc} is the short-circuit current density (mA cm⁻²), V_{oc} is the open-circuit voltage (V), P_{in} is the incident light power, and I_{mp} (mA cm⁻²) and V_{mp} (V) are the current density and voltage in the current-voltage (I - V) curves, respectively, at the point of maximum power output (P_{\max}). The I - V curves are shown in Figure 7, and the cell parameters corresponding to these DSSCs are summarized in Table III.

The addition of IL-SiO₂ brought a significant improvement in I_{sc} . This could be attributed to the formation of a new ion-transportation method caused by the nanocomposite SiO₂, which promoted the movement of free ions in a regular direction.³³ At the microscopic level, it maintained a liquidlike structure, which was important for sufficient conductivity.³¹ However, I_{sc} decreased with further amount of modified SiO₂. This was mainly because the high-density Si-O-Si network formed in the PVDF matrix decreased the porosity of the polymer membrane and hindered the charge transfer. The variable trend of I_{sc} could also be recognized from the variation of the apparent D , as

indicated in Table II. The diffusion of triiodide (D) played a major role in the DSSC performance.³⁴ The faster transportation speed of the triiodide led to the faster reduction of I⁻ and, as a result, the faster reduction of the excited dye molecule. With the increase of the modified SiO₂, the apparent D first increased and then decreased with a high peak of 2.54×10^{-6} cm²/s. The cell using a GPE of PVDF/IL-SiO₂ (8 : 2 m/m) showed a preferable photovoltaic performance, with about a 70% efficiency of DSSC using liquid electrolyte, because of a higher D . However, because of the poor D when too much IL-SiO₂ was added, the cell had a very low short current and a low energy conversion efficiency.

CONCLUSIONS

A new type of IL-SiO₂ was synthesized and characterized. A GPE based on PVDF/IL-SiO₂ was prepared by the soaking of a porous membrane in an organic electrolyte solution containing the I⁻/I₃⁻ redox couple. IL-SiO₂ improved the compatibility with liquid electrolyte and polymer matrix for its ionic liquid characteristics. The electrolytes prepared with these new nanoparticles improved cell performance by increasing I_{sc} , presumably through the creation of specific pathways for ion transportation. A DSSC using a GPE of PVDF/IL-SiO₂ (8 : 2 m/m) yielded a V_{oc} of 0.662 V, a short-circuit current of 13.40 mA/cm², and a conversion efficiency of 4.01% at 1 sun illumination. The optimization of the proportion of SiO₂ and imidazolium iodide moieties is under study, and we expect to make full use of the inherent properties of the ionic liquid.

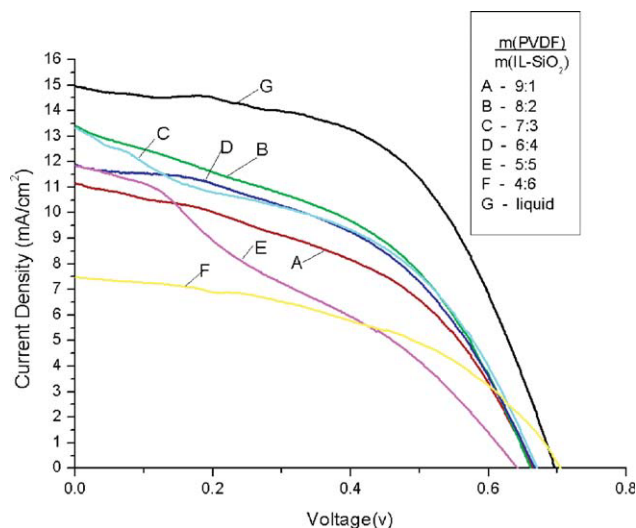


Figure 7 I - V curves of DSSCs fabricated from various GPEs at 1 sun illumination. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

TABLE III
 Photovoltaic Performance of the DSSCs

Cell	V_{oc} (V)	I_{sc} (mA/cm ²)	ff	η (%)
A	0.664	11.16	0.459	3.40
B	0.662	13.40	0.451	4.01
C	0.671	13.34	0.435	3.89
D	0.667	11.89	0.481	3.81
E	0.643	11.84	0.311	2.37
F	0.705	7.484	0.468	2.47
G	0.697	14.95	0.549	5.72

References

1. Grätzel, M. *Nature* 2001, 414, 338.
2. Bandara, J.; Weerasinghe, H. *Sol Energy Mater Sol Cells* 2005, 85, 385.
3. Xia, J.; Masaki, N.; Lira-Cantu, M. *J Am Chem Soc* 2008, 130, 1258.
4. Xue, B.; Wang, H.; Hu, Y. *C R Chim* 2006, 9, 627.
5. Zafer, C.; Ocakoglu, K.; Ozsoy, C. *Electrochim Acta* 2009, 54, 5709.
6. Guo, L.; Pan, X.; Zhang, C. N. *Sol Energy* 2010, 84, 373.
7. Li, B.; Lin, J. M.; Li, S. Q. *Mater Rev* 2008, 22, 106.
8. Bandaraa, T.; Dissanayakea, M.; Albinssonb, I. *J Power Sources* 2010, 195, 3730.
9. Benedetti, J. E. *J Power Sources* 2010, 195, 1246.
10. Grätzel, M. *J Photochem Photobiol A* 2004, 164, 3.
11. Berginca, M. *Thin Solid Films* 2008, 516, 4645.
12. Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *J Fluorine Chem* 2004, 125, 1241.
13. Stathatos, E.; Lianos, P.; Zakeeruddin, S. M.; Liska, P.; Grätzel, M. *Chem Mater* 2003, 15, 1825.
14. Stathanos, E.; Lianos, P.; Jovanovski, V.; Orel, B. *J Photochem Photobiol A* 2005, 169, 57.
15. Cerneaux, S.; Zakeeruddin, S. M.; Pringle, J. M.; Cheng, Y. B.; Grätzel, M.; Spiccia, L. *Adv Funct Mater* 2007, 17, 3200.
16. Mizumo, T.; Watanabe, T.; Matsumi, N.; Ohno, H. *Polym Adv Technol* 2008, 19, 1445.
17. Kato, T.; Okazaki, A.; Hayase, S. *Chem Commun* 2005, 363.
18. Usui, H.; Matsui, H.; Tanabe, N.; Yanagida, S. *J Photochem Photobiol A* 2004, 164, 97.
19. Fang, G.; Chen, J.; Wang, J.; He, J.; Wang, S. *J Chromatogr A* 2010, 1217, 1567.
20. Lai, G.; Peng, J.; Li, J.; Yang Yan, Tao Jie, Jin Xin, Qin Qi. *Tetrahedron Lett* 2006, 47, 6951.
21. Tanielian, C. *Coord Chem Rev* 1998, 178, 1165.
22. Anandan, S.; Pitchumani, S.; Muthuraaman, B.; Maruthamuthu, P. *Sol Energy Mater Sol Cells* 2006, 90, 1715.
23. Tao, H. J.; Tao, J.; Wang, T.; Wang, L.; Qin, L.; Xu, L.-L. *Trans Nonferrous Met Soc China* 2005, 15, 462.
24. Lavrencic-Stangar, U.; Groselj, N.; Orel, B.; Colomban, P. *Chem Mater* 2000, 12, 3745.
25. Saito, Y.; Stephan, A. M.; Kataoka, H. *Solid State Ionics* 2003, 160, 149.
26. Chunga, N. K.; Kwonb, Y. D.; Kim, D. *J Power Sources* 2003, 124, 148.
27. Kim, K.; Park, N.-G.; Ryu, K.-S.; Chang, S.-H. *Electrochim Acta* 2006, 51, 5636.
28. Jeon, J.-D.; Kim, M.-J.; Kwak, S.-Y. *J Power Sources* 2006, 162, 1304.
29. Hodge, R. M.; Edward, G. H.; Simon, G. P. *Polymer* 1996, 37, 1371.
30. Liu, Y.; Lee, J. Y.; Hong, L. *J Power Sources* 2004, 129, 303.
31. Anandan, S.; Sivakumar, R. *Phys Status Solidi A* 2009, 206, 343.
32. Kontos, A. G.; Fardis, M.; Prodromidis, M. I.; Stergiopoulos, T.; Chatzivasiloglou, E.; Apavassiliouc, G.; Falaras, P. *Phys Chem Chem Phys* 2006, 8, 767.
33. Xiang, W. C.; Zhou, Y. F.; Yin, X.; Zhoua, X. W. *Electrochim Acta* 2009, 54, 4186.
34. Asano, T.; Kubo, T.; Nishikitani, Y. *J Photochem Photobiol A Chem* 2004, 164, 111.