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# Composite electrolytes based on poly(ethylene oxide) and binary ionic liquids for dye-sensitized solar cells

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The sunlight is the largest single available source of clean and renewable energy to ensure human society's sustainable development. Owing to their low production cost and high energy conversion efficiency, dye-sensitized solar cells (DSSCs) have been regarded as good alternatives to conventional photovoltaic devices. Herein, a series of composite electrolytes based on poly(ethylene oxide) (PEO) and the binary ionic liquids 1-propyl-3-methy-imidazolium iodide ([PMIm]I) and 1-ethyl-3methylimidazolium thiocyanate ([EMIm][SCN]) were prepared and then applied to fabricate six DSSCs. The composite electrolytes were characterized by fourier transform infrared spectroscopy (FTIS), X-ray diffraction (XRD), and electrochemical impedance spectra (EIS). It was shown that the addition of binary ionic liquids would reduce the degree of crystallinity of PEO, thus improving the ionic conductivities of the electrolytes by about 2 orders of magnitude. Investigation on the photovoltaic performances of these DSSCs showed that the fill factor (*FF*) could reach up to 0.67 and energy conversion efficiency ( $\eta$ ) could reach up to 4.04% under AM 1.5 full sunlight (100 mW/cm<sup>2</sup>).

solar energy, dye-sensitized solar cell, PEO, binary ionic liquid, composite electrolyte

# 1 Introduction

With the global economy slowly and steadily recovering from the financial crisis, world energy consumption will grow by 53%, from about 41 trillion watts (TW) in 2008 to about 62.5 TW in 2035. Accordingly,  $CO_2$  emissions produced from the combustion process will rise from 30.2 billion metric tons to 43.2 billion metric tons over the same period [1]. If this continues, we and our future generations will find ourselves trapped on the planet with an irreversible depletion of fossil resources and inevitable damage to global climate [2]. So we must find and utilize some clean, renewable energy sources to ensure the sustainable development of human society. Solar radiation is the best ecological [3] and the largest available source of clean energy, it deposits 120,000 TW of electromagnetic radiation on the earth [4]. If we could recover 0.50% of the radiation with 10% efficient solar-conversion systems, there would be about 60 TW of power, enough to meet our energy demand. However, only about 5 GW power is generated from solar energy by photovoltaic devices so far [5]. Thus, there is a huge gap between our present use of solar energy and its enormous undeveloped potential [2].

Dye-sensitized solar cells (DSSCs) have been regarded as a bridge for this huge gap. Since they were firstly presented in 1991 by Grätzel [6] based on the principle of mimicking natural photosynthesis, DSSCs have already attracted considerable attention and are seen as good alternatives to conventional photovoltaic devices because of their low production cost and high energy conversion efficiency [7–9]. It was reported that DSSCs based on organic solvents had been prepared with conversion efficiency reaching up to 11.18% [10]. However, organic solventbased electrolytes generate difficulties such as leakage and

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evaporation [11, 12], which limit the long-term stability and outdoor application of these cells [13–15]. Therefore, much research has been done to replace the volatile solvents with polymer [16-19] or gel electrolytes [20-22]. Because of their excellent physicochemical properties such as non-volatility, non-flammability, and high ionic conductivity, ionic liquids have been added to improve the stability and ionic conductivity of the polymer/gel electrolytes [3, 7, 23-27]. It has been reported that solar cells fabricated with composite electrolytes based on poly(ethylene oxide) (PEO) and the ionic liquid (1-ethyl-3-methylimidazolium dicyanamide, [EMIm][DCN]) showed an improved efficiency of 2%, almost doubled that of DSCCs fabricated with electrolytes without ionic liquids (1.04%) [19]. From the result, we can see that although the substitution of organic solvents with a single ionic liquid could solve the stability issues, a shortage of the electrolytes might result in low conversion efficiency. In order to combine the stability of the electrolytes and high conversion efficiency, we prepared a series of composite electrolytes based on a pure PEO sample and the binary ionic liquids [PMIm]I and [EMIm][SCN]. The obtained composite electrolytes were then characterized by FTIR, XRD, and EIS. The photovoltaic performances of the solar cells fabricated with these composite electrolytes were also investigated, with the fill factor (FF) reaching up to 0.67 and the energy conversion efficiency ( $\eta$ ) up to 4.04% under AM 1.5 full sunlight ( $100 \text{ mW/cm}^2$ ).

# 2 Experimental

## 2.1 Characterization techniques

FTIR spectra were recorded with an Equinox-55 FTIR spectrometer (Bruker) with a wave number resolution of 2 cm<sup>-1</sup> in the frequency range from 4000 to 400 cm<sup>-1</sup>. <sup>1</sup>H NMR spectra were obtained on a Bruker AVANCE Digital 400 NMR spectrometer. The spectra were recorded at 25 °C in DMSO solution using TMS as an external reference. X-ray diffraction data were collected on a Dmax/IIIA diffractometer (Rigaku) in the  $2\theta$  range of  $10^{\circ}$ – $40^{\circ}$  with a scan rate of 1°/min at room environmental conditions. Electrochemical impedance spectra of DSSCs were measured using an IM6ex electrochemical workstation (Zahner). The spectra were scanned in a frequency range of 0.1-100,000 Hz at room temperature. The open-circuit voltage ( $V_{OC}$ ), shortcircuit current density  $(J_{SC})$ , fill factor (FF), and total energy conversion efficiency  $(\eta)$  of DSSCs used in the study were obtained through the current voltage characteristics at room temperature. These were monitored and recorded using a Keithley 2420 source meter under a solar simulator (Xenon lamp, Changchun Institute of Optics Fine Mechanics and Physics, Chinese Academy of Sciences, calibrated versus the solar spectrum, AM 1.5, 100 mW/cm<sup>2</sup>).

#### 2.2 Synthesis and characterization of ionic liquids

[PMIm]I was prepared according to ref. [28] and characterized by <sup>1</sup>H NMR. The results were as follows: <sup>1</sup>H NMR (400 MHz, [D6]DMSO, TMS):  $\delta = 9.82$  (s, 1H), 7.56 (d, 1H), 7.51 (d, 1H), 4.26 (t, 2H), 4.06 (s, 3H), 1.92 (m, 2H), 0.94 (t, 3H). [EMIm][SCN] was synthesized in two steps according to ref. [29]. First, 16.35 g ethylbromide (0.15 mol) was slowly added to 9.02 g N-methylimidazole (0.11 mol) under stirring conditions. The mixture was further stirred for 24 h at ambient temperature. After separation from the mixture, the viscous [EMIm]Br phase was washed with 1,1,1-trichoroethane (30 mL  $\times$  3), and then dried at 80 °C under vacuum. Second, 7.60 g NH<sub>4</sub>[SCN] (0.10 mol) was added to 200 mL acetonitrile containing 19.10 g [EMIm]Br (0.10 mol) and stirred for 8 h. After the removal of the NH<sub>4</sub>Br precipitate and the remaining acetonitrile, the ionic liquid of [EMIm][SCN] was obtained and further dried at 80 °C in vacuum. <sup>1</sup>H NMR (400 MHz, [D6]DMSO, TMS):  $\delta$  = 8.64 (s, 1H), 7.42 (d, 1H), 7.26 (d, 1H), 4.10 (s, 3H), 1.66 (m, 2H), 1.30 (t, 3H).

### 2.3 Preparation of electrolytes

The binary ionic liquids-PEO-based electrolytes were prepared by the solution casting method [16]. The ratio of [PMIm]I to the whole electrolyte was fixed to 20 wt% and it was 2 wt% for I<sub>2</sub>. In a series of electrolytes, the ratios of [EMIm][SCN] were set as 0, 10, 20, 30, 40, and 50 wt%, respectively, and the corresponding amounts of PEO were set as 78, 68, 58, 48, 38, and 28 wt%. The obtained six electrolytes are coded as a, b, c, d, e, and f, respectively. The stoichiometric amounts of [PMIm]I, PEO, and I2 were dissolved in acetonitrile at room temperature, then [EM-Im][SCN] was added under vigorous agitation for 4 h to form a viscous homogeneous solution. The solution was dried at 40 °C for 48 h under reduced pressure to remove acetonitrile and afford the film-wise electrolytes. In the extended experiments, we found that it was difficult to get a stable film when the concentration of [EMIm][SCN] exceeded 60 wt%.

### 2.4 DSSCs fabrication and photovoltaic experiments

Electrode preparation [30]: 20 mL ethanol was slowly added to 35 g Nano TiO<sub>2</sub> powder (P25) under continuous mechanical stirring, resulting in the formation of a homogeneous paste. The homogeneous TiO<sub>2</sub> paste was then coated on transparent conductive oxide-coated glass electrodes by the doctor-blade technique. In order to have the TiO<sub>2</sub> paste make good contact with the glass electrodes, the electrodes were pre-treated with 50 mM TiCl<sub>4</sub> for 30 min at 70 °C. After being coated, the electrodes were then dried at 60 °C for 4 h in vacuum to afford TiO<sub>2</sub>-coated electrodes ready for use. N719 (0.7503 g) was weighed and dissolved in ethanol to get a dye solution of 3.001 g/L. Chenodeoxycholic acid (CDCA) was added to the solution to prevent the dye molecules from agglomerating on the surface of the TiO<sub>2</sub>. The TiO<sub>2</sub> electrode was sensitized in the dye solution for 2 h and then flushed with ethanol and dried at room temperature. The sensitized TiO<sub>2</sub> electrode should be kept in desiccators and away from moisture and Fe to avoid the failure of the dye. To prepare the counter electrode, a drop of 5 mM H<sub>2</sub>PtCl<sub>6</sub>·H<sub>2</sub>O in 2-propanol was placed on the FTO glass substrate with a small pre-drilled hole, followed by drying and annealing at 450 °C for 30 min. The sensitized TiO<sub>2</sub> electrode and the counter electrode were assembled into a sealed sandwich-type cell with a Surlyn film (DHS-SN1725/1760) in the middle. The cell was filled with the prepared electrolytes through the pre-drilled small hole under reduced pressure. Finally, the small hole was sealed with Surlyn film and a cover glass. In the photovoltaic experiments, the active area of the cells was fixed to  $0.15 \text{ cm}^2$ . The photovoltaic characterization of the DSSCs was done under standard conditions by illumination of AM 1.5 global radiation with 100 mW/cm<sup>2</sup> light intensity.

# 3 Results and discussion

# 3.1 FTIR analysis of ionic liquids

The FTIR spectra of [PMIm]I and [EMIm][SCN] are shown in Figure 1. FTIR spectrum of [PMIm]I: The peak at 3138 cm<sup>-1</sup> could be assigned as stretching of the C–H bond in the imidazolium ring. A band of 3080 cm<sup>-1</sup>, the so-called "Cl interaction band" in some literature [31], was attributed to the H-bond interactions between the C–H groups on the cations and anions [32], while a peak of 823 cm<sup>-1</sup> was reported as the out-of-plane bending modes of a rather strong C–H bond. The bands of 2964 and 2880 cm<sup>-1</sup> were attributed to double CH<sub>2</sub> stretching vibrations. The other peaks at 1570, 1460, 1160, and 746 cm<sup>-1</sup> were ascribed to stretching of ring (C–C) bonds [33], asymmetric bending of CH<sub>3</sub>, stretching of CH<sub>3</sub>–N [34], and stretching of methyl C–H bonds on the cations, respectively.

FTIR spectrum of [EMIm][SCN]: The peaks at 3138, 1571, 1459, 1167, 839, and 749 cm<sup>-1</sup> in [EMIm][SCN] correspond almost exactly to the peaks at 3138, 1570, 1460, 1160, 823, and 746 cm<sup>-1</sup> in [PMIm]I because the two ionic liquids share the same skeleton imidazolium rings and are only different in the 3-substituent group. The peaks at 3096, 2056 cm<sup>-1</sup> were ascribed to the absorption of thiocyanate ([SCN]<sup>-</sup>) and the band of 617 cm<sup>-1</sup> was assigned as the stretching vibration of C–S [33].

### 3.2 FTIR studies of composite electrolytes

FTIR spectra of composite electrolytes  $\mathbf{a}$ - $\mathbf{f}$  are shown in Figure 2. It has been reported that there were several characteristic vibrations of the pure PEO sample: a CH<sub>2</sub> stretch-



Figure 1 FTIR spectra of [PMIm]I and [EMIm][SCN].



Figure 2 FTIR spectra of composite electrolytes.

ing in the wavenumbers of 2935–2800 cm<sup>-1</sup> (especially at 2891 cm<sup>-1</sup> [35] and 2885 cm<sup>-1</sup> [36] for different molecular weight samples), a C–O–C stretching vibration in the wavenumbers of 1250–950 cm<sup>-1</sup> (especially at 1114 cm<sup>-1</sup> [37] and 1101 cm<sup>-1</sup> [35]), a CH<sub>2</sub> twisting vibration at 961 cm<sup>-1</sup>, and a CH<sub>2</sub> wagging vibration at 841 cm<sup>-1</sup> [35].

From Figure 2, it is clear that all the characteristic vibrations of the pure PEO sample mentioned above can be found in the FTIR spectra of the six electrolytes (about 2885, 1098, 957, and 843 cm<sup>-1</sup>). Among them, the typical absorption band at about 2885 cm<sup>-1</sup> is found to overlap with the absorption bands of [PMIm]I at 2964 and 2880 cm<sup>-1</sup>. As for the C–O–C stretching vibration, it is observed to be red-shifted from 1114 cm<sup>-1</sup> of the pure PEO sample to 1098 cm<sup>-1</sup> in all composite electrolytes. The red-shift can be ascribed to the formation of a transient cross-linking complex between the cations of the ionic liquids and the ether oxygen of the PEO, so that the generated transition state will weaken the C–O–C stretching vibration and the crystallization of PEO will be decreased [37]. The characteristic absorption bands of [EMIm][SCN] at 3096 and 2056 cm<sup>-1</sup> are also found to appear in the FTIR spectra of all electrolytes doped with it (**b**, **c**, **d**, **e**, **f**), while the bands of 3140, 1162, and 617 cm<sup>-1</sup> are detectable only in the composite electrolytes such as **e** and **f**, which contain higher amounts of the binary ionic liquids.

#### 3.3 XRD studies of six composite electrolytes

Figure 3 presents the XRD patterns of PEO and the six composite electrolytes **a-f**. There are two sharp peaks at 19.2° and 23.4° in the pure PEO sample, which implies that pure PEO has a high degree of crystallinity. In accordance with the pure PEO sample, no new peaks appeared in any of the composite electrolytes, but the intensities of the related peaks decreased rapidly with the increasing amounts of the binary ionic liquids. When the amount of [EMIm][SCN] reached 50 wt% (and the total amount of the binary ionic liquids reached 70 wt%), the two characteristic peaks of PEO almost disappeared. This phenomenon indicated that the introduction of the binary ionic liquids led to a lower degree of crystallinity of PEO and thus resulted in higher ionic conductivity (the results are shown in Table 1), although the decreased amount of PEO in the electrolytes also contributes to the declined intensity of the diffraction peak.

The crystalline reduction of the PEO sample doped with binary ionic liquids is probably a result of the interruption of PEO–PEO interactions, which is caused by the formation of hydrogen bonds between the ether groups of PEO and N–CH<sub>3</sub> on the cations of binary ionic liquids [36]. Here, the red shift of the band at 1114 cm<sup>-1</sup> in the FTIR spectra of the composite electrolytes also confirms this conclusion. Beyond this, it has been reported that the composition of PEO and some salts could result in a significant interfacial area in PEO, which would not only reduce the crystallinity of the PEO sample but also sustain the mechanical properties of a semi-crystalline PEO-based electrolyte [38].

### 3.4 EIS analysis of composite electrolytes

The ionic conductivities of the composite electrolytes obtained by electrochemical impedance spectroscopy are listed in Table 1. It can be seen that the ionic conductivity ( $\sigma$ ) increases with increasing amounts of [EMIm][SCN], gradually rising from 7.40 × 10<sup>-6</sup> S m<sup>-1</sup> to the maximum of 1.63 × 10<sup>-4</sup> S m<sup>-1</sup>, while the ionic conductivity of the pure PEO sample (MW  $\approx 3 \times 10^5$ ) is about 1.2 × 10<sup>-7</sup> S m<sup>-1</sup> at room



**Figure 3** XRD patterns of the pure PEO sample and composite electrolytes.

temperature [38]. These results suggest that the ionic conductivities of the electrolytes are improved by about 2 orders of magnitude by introducing binary ionic liquids into the pure PEO sample. The introduction of more free ions ([PMIm]<sup>+</sup>,  $\Gamma$ , [EMIm]<sup>+</sup>, and [SCN]<sup>-</sup>) might be one reason for the improved ionic conductivity. In addition, the crystalline reduction of all composite electrolytes means an elevated amount of the amorphous phase in the polymer matrix, which enhances the ionic mobility of free ions [39], thus improving the ionic conductivities of composite electrolytes.

# 3.5 Photovoltaic performances of DSSCs fabricated with composite electrolytes

DSSCs fabricated with electrolytes **a**, **b**, **c**, **d**, **e**, **f** are coded as **A**, **B**, **C**, **D**, **E**, **F**, respectively. The photovoltaic performances of all the DSSCs **A**–**F** are shown in Figure 4 and listed in Table 2 in detail.

The photovoltaic performances show that the total energy conversion effiency is just 1.40% using DSSC **A** as a photovoltaic device (with electrolytes a, PEO:[PMIm]I:I<sub>2</sub> = 78:20:2) in full AM 1.5 sunlight, which is only slightly higher than the result previously reported ( $\eta = 1.04\%$  with similar electrolytes as in PEO:KI:I<sub>2</sub> = 75:25:2.5) in the literature [19]. It is interesting to see that the ionic conductivities ( $\sigma$ ) of composite electrolytes are improved by about 2 orders of magnitude with increasing amounts of binary ionic liquids (more free ions) and with the decreasing crystallinity of the PEO-based electrolytes (better ionic mobility). Accordingly, the total energy conversion efficiency ( $\eta$ ) of these DSSCs is increased from 1.40% (DSSC **A**) to 3.08% (DSSC **E**). DSSC **F** in particular gives a conversion efficiency of 4.04% with  $V_{OC}$ ,  $J_{sc}$ , and *FF* be-

**Table 1** The contents <sup>a)</sup> and ionic conductivities ( $\sigma$ ) of electrolytes **a**-**f** 

Electrolytes	PEO (wt%)	[EMIm][SCN] (wt%)	Conductivity (S/m)
а	78	0	$7.40 \times 10^{-6}$
b	68	10	3.10×10 <sup>-5</sup>
c	58	20	3.47×10 <sup>-5</sup>
d	48	30	$1.06 \times 10^{-4}$
e	38	40	$1.14 \times 10^{-4}$
$\mathbf{f}^{b)}$	28	50	$1.63 \times 10^{-4}$

a) The contents of [PMIm]I and  $I_2$  are fixed as 20 wt% and 2 wt%, respectively; b) in later experiments, it was hard to get a stable film when the contents of [EMIm][SCN] exceeded 60 wt%.

Table 2 Photovoltaic performances<sup>a)</sup> of DSSCs<sup>b)</sup> fabricated with the six electrolytes

DSSCs	$V_{\rm OC}(V)$	$J_{\rm SC} ({\rm mA/cm}^2)$	$P_{\rm max}~({\rm mW/cm}^2)$	FF	η (%)
Α	0.66	4.07	1.40	0.52	1.40
В	0.66	5.27	2.21	0.63	2.21
С	0.73	5.34	2.61	0.67	2.61
D	0.70	6.32	2.84	0.64	2.84
Е	0.70	8.99	3.08	0.49	3.08
F	0.78	7.70	4.04	0.67	4.04

a) The input light intensity,  $P_{\rm in} = 100 \text{ mW/cm}^2$ ;  $V_{\rm oc}$ : open circuit photovoltage;  $J_{\rm sc}$ : short circuit photo-current density;  $P_{\rm max}$ : maximum electrical output power density; FF: fill factor ( $FF = P_{\rm max}/V_{\rm oc}J_{\rm sc}$ );  $\eta$ : total energy conversion efficiency ( $\eta = P_{\rm max}/P_{\rm in}$ ); b) the active area of all the DSSCs is fixed to 0.15 cm<sup>2</sup>.

ing 0.78 V, 7.70 mA/cm<sup>2</sup>, and 0.67, respectively.

# 4 Conclusions

A series of novel composite electrolytes based on PEO and binary ionic liquids were prepared and applied for the fabrication of six DSSCs. The composite electrolytes were characterized by FTIR, XRD, and EIS. It was shown that the addition of binary ionic liquids would reduce the degree of crystallinity and improve the ionic conductivities of these composite electrolytes by about 2 orders of magnitude. The photovoltaic performances of these DSSCs showed that the total energy conversion efficiency was also improved with increasing amounts of binary ionic liquids, and finally, a DSSC was obtained with a fill factor up to 0.67 and a conversion efficiency up to 4.04% under AM 1.5 full sunlight (100 mW/cm<sup>2</sup>). Thus, these DSSCs fabricated with PEO and binary ionic liquids would have great potential to facilitate the future utilization of solar energy.

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