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# Ionic Liquid Based Electrolytes for Dye-Sensitized Solar Cells

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## 1. Introduction

### 1.1 New type of solar cell: dye-sensitized solar cells (DSSCs)

The rising price of fossil fuels, together with their rapid depletion and the pollution caused by their combustion, is forcing us to find sources of clean renewable energy. Fortunately, the supply of energy from the sun to the earth is gigantic, i.e.,  $3 \times 10^{24}$  joule a year or about ten thousand times more than what mankind consumes currently. This means that only 0.1% of the earth's surface with solar cells with an efficiency of 10% would suffice to satisfy our current needs (Hamakawa, 2004; Grätzel, 2001). Therefore, solar power is considered to be one of the best sustainable energies for future generations. There are already a number of terrestrial applications where photovoltaic devices provide a viable means of power generation. Photovoltaic devices are based on the concept of charge separation at an interface of two materials of different conduction mechanism. To date photovoltaics has been dominated by solid-state junction devices, usually in silicon, crystalline or amorphous, and profiting from the experience and material availability resulting from the semiconductor industry. However, the expensive and energy-intensive high-temperature and high-vacuum processes is needed for the silicon based solar cells. Therefore, the dominance of the photovoltaic field by such kind of inorganic solid-state junction devices is now being challenged by the emergence of a third generation of solar cell based on interpenetrating network structures, such as dye-sensitized solar cells (DSSCs) (Grätzel, 2001; O'Regan *et al.*, 1991).

DSSCs have been extensively investigated since O'Regan and Grätzel reported a 7.1% solar energy conversion efficiency in 1991 (O'Regan *et al.*, 1991). DSSCs offer particular promise as an efficient, low cost alternative to Si semiconductor photovoltaic devices and represent a specific type of photoelectrochemical cell. The advantages of DSSCs are that they do not rely on expensive or energy-intensive processing methods and can be printed on flexible substrates using roll-to-roll methods. Instead of using a single crystal semiconductor, DSSCs rely on a thin mesoporous film (10-15  $\mu\text{m}$  thick) of nanocrystals of a metal oxide, most often  $\text{TiO}_2$ , which is sensitized to visible light with a molecular light absorber. The sensitized nanoparticles are combined with a redox active electrolyte solution and counter electrode to produce a regenerative photoelectrochemical cell. By using the traditional liquid electrolyte, the DSSC has achieved an 11.5% efficiency record (Chen *et al.*, 2009), encouraging the surge to explore new organic materials for the conversion of solar to electric power. However, presence of liquid electrolytes in traditional DSSCs has some problems such as a less long-

term stability and a need for hermetic sealing due to the leakage and evaporation of the organic solvent (Chen *et al.*, 2010; Lee *et al.*, 2010a & 2010b). In this review, we pay particular attention on the recent development of quasi-solid-state and all-solid-state DSSCs using ionic liquid (IL) electrolytes. The problems researchers have encountered and the prospects of DSSCs are also discussed.

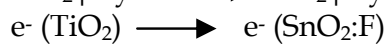
## 1.2 The structure and operational principle for DSSCs

A schematic presentation of the structure of a DSSC is given in Fig. 1. A typical DSSC is composed of two sheets of glass coated with a transparent conductive oxide layer. One of the glass plates (the working electrode) is covered with a film of small dye-sensitized semiconductor particles; The large surface area of the nanoparticles, which is as much as a factor of 1,000 greater than the geometric area of the film, allows a monolayer of surface-bound dye to absorb nearly all of the incident sunlight in the region of the spectrum where the dye absorbs. The other glass plate (the counter-electrode (CE)) is coated with a catalyst. Two electrodes are sandwiched together and the electrolyte, typically containing the iodide/triiodide ( $I^-/I_3^-$ ) redox couple in an organic solvent, fills the gap between them. The basic sequence of events in a DSSC is as follows:

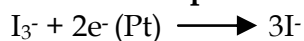
### Activation



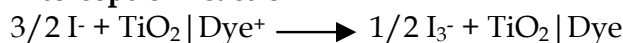
### Electron injection



### Electron reception



### Interception reaction



Upon absorption of light, an electron is injected from a metal-to-ligand charge transfer excited state of the dye into the conduction band of the metal oxide. The rate of this electron injection reaction is ultrafast, typically occurring on the order of hundreds of femtoseconds to tens of picoseconds. The injected electron percolates through the  $TiO_2$  film, and is thought to move by a "hopping" mechanism and is driven by a chemical diffusion gradient (rather than an electric field), and is collected at a transparent conductive substrate of fluorine doped tin oxide glass ( $SnO_2:F$ ), on which the  $TiO_2$  film is printed. After passing through an external circuit, the electron is reintroduced into the solar cell at the platinum counter electrode, where triiodide is reduced to iodide. The iodide then regenerates the oxidized dye, thereby completing the circuit with no net chemical change.

## 1.3 The application of ionic liquids (ILs) in DSSCs

DSSCs are among the most extensively investigated devices that provide a high light-to-electric energy conversion yield. The electrolyte is one of key components for dye-sensitized solar cells and its properties have much effect on the conversion efficiency and stability of

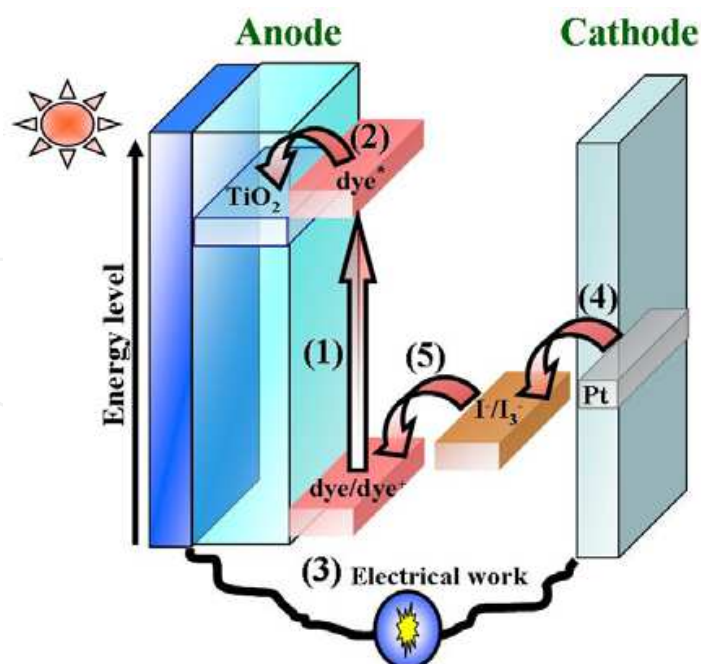


Fig. 1. Schematic diagram of structure and function of a typical  $\text{TiO}_2$  based dye-sensitized solar cell.

the solar cells. One of the critical components of DSSCs is the electrolyte containing a  $\text{I}^-/\text{I}_3^-$  redox couple that mediates the dye regeneration process. Alkylimidazolium iodides are frequently employed as the electrolyte because they can improve the photovoltaic performance of such devices (Kambe *et al.*, 2002; Kubo *et al.*, 2003). Alkylimidazolium cation may be adsorbed on the surface of semiconductor film to form the Helmholtz layer, which restricted the contact of triiodide and semiconductor films ( $\text{TiO}_2$ ), for the recombination between triiodide and electron in the conduction band of semiconductor. As the result, the fill factor and conversion efficiency of the solar cells were improved. On the other hand, the high solubility of alkyl imidazolium cation in organic solvent and the high activity of iodide increased the light harvesting efficiency and photocurrent as well as the stability of the sensitizer. The highest efficiency record of DSSC was obtained based on organic solvent electrolyte, especially the highly volatile organic solvent electrolyte due to the efficient infiltration of organic electrolyte in nanocrystalline films. However, the DSSCs based on organic electrolyte have the disadvantages such as less long-term stability, difficulty in robust sealing and leakage of electrolyte due to the volatility of organic solvent. In order to develop the DSSCs for outdoor use, we have to overcome the technological problems mentioned above. For this purpose, ILs have been considered as one of the alternative electrolytes for DSSCs and other electrochemical devices for replacing organic solvent because of their good chemical and thermal stability, negligible vapor pressure, nonflammability, wide electrochemical window, and high ionic conductivity (Fredlake *et al.*, 2004; Pringle *et al.*, 2002). Notably, 1-propyl-3-methylimidazolium iodide (PMII), an IL at room temperature with a viscosity of 880 cP, is by far the most commonly used in solvent-free ILs based electrolyte (PMII provides both iodide sources and solvents of electrolytes for DSSCs). Recently, many imidazolium salts with functional groups have been reported, and some functionalized imidazolium iodide salts have been evaluated as electrolytes in DSSCs with some success (Kambe *et al.*, 2002; Kubo *et al.*, 2003). Figure 2 summarizes the structure

and viscosity of some alkylimidazolium cations-based room temperature ionic liquids (RTILs) (Kong *et al.*, 2007).

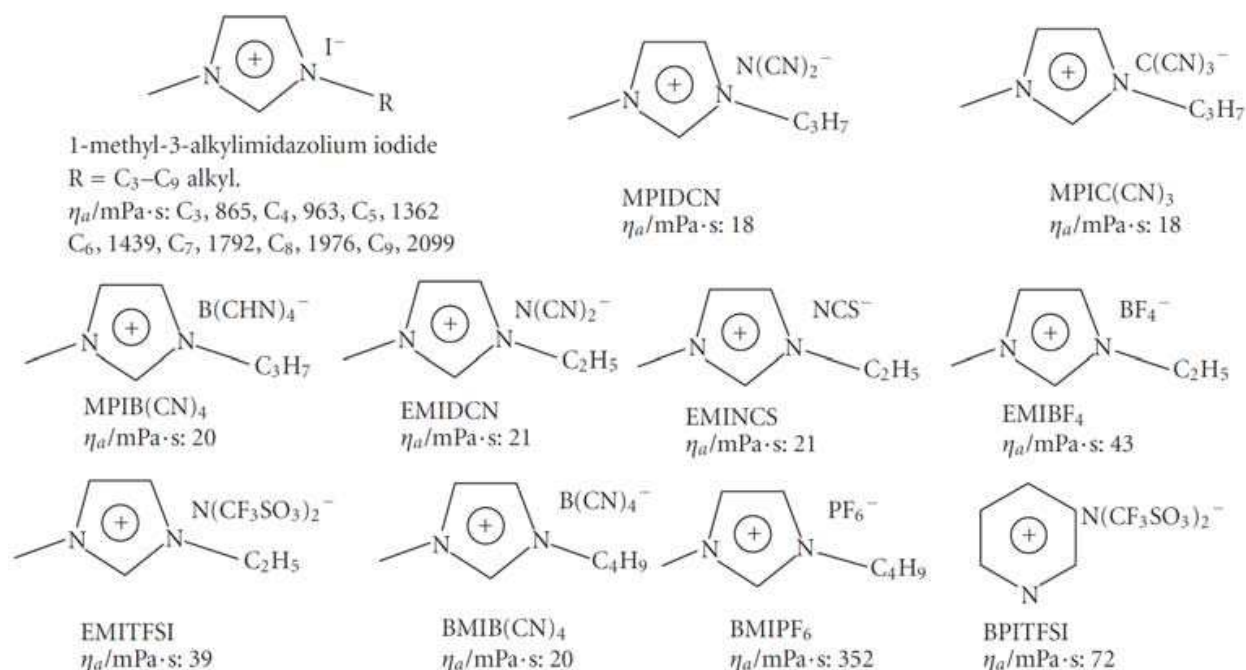


Fig. 2. Structure and the viscosity of several alkylimidazolium cations based RTILs (Kong *et al.*, 2007).

Here we scrutinize the recent advances on DSSCs using different electrolytes incorporating ILs. The IL employed in DSSC can be classified as follows: (a) a quasi-solid-state DSSC with IL served as both the source of iodide and the solvent themselves (system A: quasi-solid-state electrolyte with ILs), (b) a near-solid-state DSSC with an ionic liquid electrolyte containing nanoparticles (system B: near solid-state electrolyte with nanoparticles solidified ILs) and (c) an all-solid-state DSSC with ionic liquid crystals (system C). These electrolytes are progressively viscous enabling increased stability.

#### 1.4 Challenges

The significant limitation of DSSCs to date has been the relatively low number of choices for the electrolyte. For one, the redox couple I<sup>-</sup>/I<sub>3</sub><sup>-</sup> has proven to be quite unique: no other redox couples have been found to date that result in better cell performance, and only one gives comparable overall conversion efficiencies (Wang *et al.*, 2004b). Secondly, the use of liquid electrolyte is not ideal for commercial applications (especially the common use of acetonitrile derivatives as the solvent), due to problems with sealing, volatility, and toxicity. Therefore, solidification and quasi-solidification of DSSCs have been intensely studied with various approaches, such as using of p-type inorganic semiconductors (Kumara *et al.*, 2002; Perera *et al.*, 2003), organic hole conducting materials (Bach *et al.*, 1998; Krüger *et al.*, 2001; Krüger *et al.*, 2002), ionic gel electrolytes having a polymer or a gelator (Kubo *et al.*, 2001; Kubo *et al.*, 2002; Wu *et al.*, 2007; Ying *et al.*, 2008), and of ionic liquid electrolytes containing dispersed nano-components (Lee *et al.*, 2009a). A solid-state device has several advantages, but short of that, a gel, polymeric, or aqueous electrolyte would present a substantial improvement. However, no viable alternative to the use of a volatile organic solvent has



been found to date. Besides, imperfect filling of the dye-adsorbed porous  $\text{TiO}_2$  film by p-type inorganic semiconductors or polymers has resulted in poor efficiency for the cells. Moreover, the carrier diffusion length was limited in the case of conducting polymers due to their low conductivity.

## 2. Reviews and motivations

IL electrolytes were developed in recent year in view of the disadvantage of organic solvent electrolyte for DSSCs. Compared with traditional organic solvent electrolyte, ILs offer many advantages, such as good chemical and thermal stability, negligible vapor pressure, nonflammability, high ionic conductivity, and wide electrochemical window. Thus, ILs have been intensively pursued as alternative electrolytes for DSSCs and other electrochemical devices. In the past few years, IL electrolytes were developed rapidly. Kubo *et al.* (Kubo *et al.*, 2002) investigated the physical and physiochemical properties of 1-alkyl-3-methylimidazolium iodides (alkyl chain: C3–C9). They found that the viscosity of the ILs increases with increasing alkyl chain length because of van der Waals forces. The conductivity of the ILs decreases with increasing viscosity since the diffusion of ions in a liquid depends on its viscosity. The electrolyte with 1-hexyl-3-methylimidazolium iodide gave the highest photoelectric conversion efficiency. Among these ionic liquids, alkyylimidazolium-based ILs provide both iodide sources and solvents of electrolytes for DSSCs. The counterions in the alkyylimidazolium based ionic liquid included  $\text{I}^-$ ,  $\text{N}(\text{CN})_2^-$ ,  $\text{B}(\text{CN})_4^-$ ,  $(\text{CF}_3\text{COO})_2\text{N}^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{NCS}^-$ , and so forth. However, 1-alkyl-3-methylimidazolium iodides are viscous liquid, whose viscosity is much higher than that of organic solvent based liquid electrolyte (viscosities for ACN and MPN are 0.37 cP and 1.60 cP, respectively), the transport of  $\text{I}_3^-$  in the electrolyte is very slow, thus limiting the current density and the cell efficiency. To improve the mobility of redox couple in the electrolyte and the photovoltaic performance, various ionic liquids with low viscosity were developed (Fei *et al.*, 2006). Grätzel group reported the DSSCs based on low-viscosity ionic liquid and PMII mixture (Wang *et al.*, 2003b; Wang *et al.*, 2004a; Kuang *et al.*, 2006; Kuang *et al.*, 2007). Besides alkyylimidazolium cation, alkylpyridinium salt and trialkylmethylsulfonium-salt-based ILs were developed for electrolytes. Paulsson *et al.* (Paulsson *et al.*, 2003) obtained 3.7% photoelectric conversion efficiency for solar cells based on  $(\text{Bu}_2\text{Me})\text{SI}$  ionic liquid containing 1% iodine. Kawano *et al.* (Kawano *et al.*, 2004) reported 2% conversion efficiency in alkylpyridiniumcation-based IL. Wang *et al.* (Wang *et al.*, 2004b) achieved 7.5% efficiency in solvent-free EMISecN-based IL containing  $\text{SeCN}^-/(\text{SeCN})_3^-$  electrolyte, which is comparable with  $\text{I}^-/\text{I}_3^-$  redox couple. However, the rareness of selenium and high costs has limited its application in DSSCs. Zhao *et al.* (Zhao *et al.*, 2008) reported a solid-state DSSC utilizing imidazolium-type ionic crystal as transfer layer, and obtained a good cell efficiency of 3.1% under one sun irradiation by adopting 1-methyl-3-propylimidazolium tetrafluoroborate as a crystal growth inhibitor, lithium bis-trifluoro-methanesulfonylimide as a charge transport enhancer, and 4-tert-butylpyridine (TBP) as a carrier recombination inhibitor. As shown in their work, the cell efficiency remained 60% of the initial value after 30 days at room temperature. Besides, Ikeda *et al.* (Ikeda *et al.*, 2005) also constructed a solid-state DSSC with a poly(N-vinyl-carbazole) hole transporter mediated by an alkali iodide. They reached a cell efficiency of 2.0% under one sun irradiation, but without the incorporation of volatile components (TBP, iodine) in their devices. On their further study (Ikeda *et al.*, 2006), a clay-like conductive composite which contained only polyaniline-

loaded carbon black (PACB) particles and an ethyleneoxide-substituted imidazolium iodide was used as composite electrolyte; the corresponding quasi-solid-state DSSC showed a cell efficiency of 3.48% under one sun irradiation. Besides, a new class of solid-state ionic conductor with a carbazole-imidazolium cation was synthesized by Midya *et al.* and investigated for application in all-solid-state DSSCs (Midya *et al.*, 2010). This kind of solid-state electrolyte containing the designed solid-state ionic conductor and iodine provide dual channels for hole/triiodide transportation, giving rise to a conversion efficiency of 2.85% under one sun irradiation.

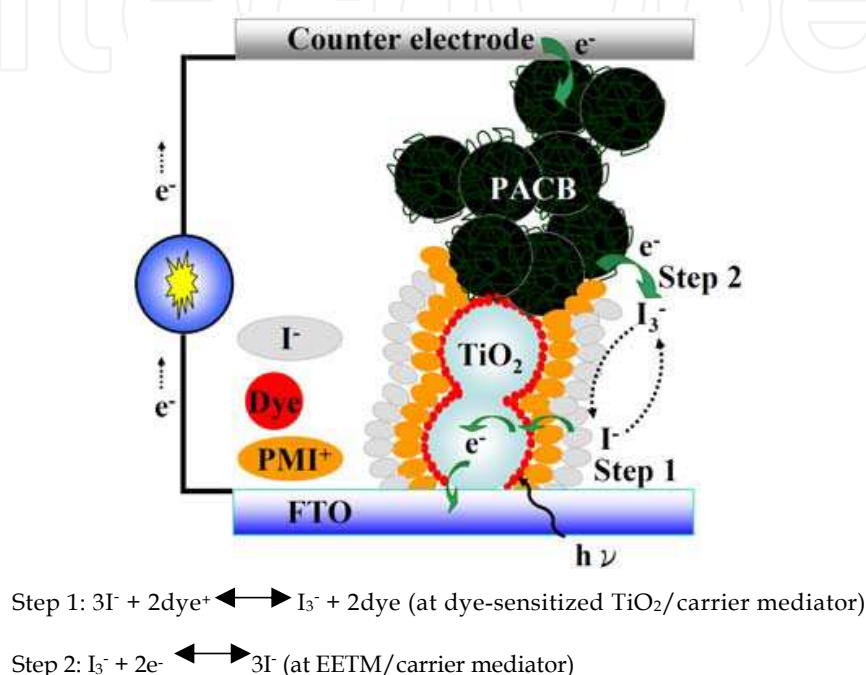


Fig. 3. The charge-transport process in a DSSC with a quasi-solid-state composite electrolyte containing an IL and PACB (Lee *et al.*, 2010a).

In the following discussions, our previous works are classified into three systems and reviewed to cover ILs-based DSSCs with good durability. In the first one (system A) (Lee *et al.*, 2009b), we compared the physicochemical properties of different structures of ILs such as 1-alkyl-3-methylimidazolium tetrafluoroborate containing various alkyl side chain lengths (alkyl chains used having the chemical formula  $\text{C}_n\text{H}_{2n+1}$ , where  $n=2, 4, 6, 8$ ), and 1-butyl-3-methylimidazolium salts containing various anions such as  $\text{BF}_4^-$ ,  $\text{PF}_6^-$  and  $\text{SO}_3\text{CF}_3^-$  on the cell performance at room temperature. An electrochemical impedance spectra (EIS) technique is also used to analyze the charge transport resistances in DSSCs, and further fit the data in Nyquist plot and calculate the exact time constant of the electrons in DSSCs, so as to understand the effect of various ILs in DSSCs. In the second system (system B) (Lee *et al.*, 2010a), we developed a quasi-solid-state DSSC with a non-volatile composite electrolyte, comprising PACB and the IL, PMII, without adding iodine. The structure of the DSSC with this kind of non-volatile composite electrolyte is shown in Figure 3. A higher cell efficiency could be achieved with the same composite electrolyte with the addition of EMISCN (1-ethyl-3-methylimidazolium thiocyanate). It is expected that PACB could form an extended electron transfer material (EETM) to reduce the diffusion length for  $\text{I}^-$  and  $\text{I}_3^-$  ions in the electrolyte, and also simultaneously serves as a charge-transporter and a catalyst for  $\text{I}_3^-$ .

reduction. Thus ultimately an iodine-free, cost-effective, efficient, and durable quasi-solid-state DSSC could be fabricated. Besides, iodine-free electrolyte is desirable for flexible metal-based DSSCs where a metal substrate, such as titanium is prone to corrosion by iodine. For the third one (system C) (Lee *et al.*, 2010b), we reported the fabrication of an all-solid-state DSSC with a hybrid SWCNT-binary charge transfer intermediate (CTI), consisting of single wall carbon nanotubes (SWCNT), EMII and PMII, without the addition of iodine and TBP. It is expected that the SWCNTs in the composite electrolyte serves simultaneously as the filler for physical gelation of electrolyte and as the catalyst for electrochemical reduction of  $I_3^-$ . Moreover, we utilized 1-methyl-3-propylimidazolium iodine (PMII), which acts simultaneously as a co-charge transfer intermediate and crystal growth inhibitor, to further improve the cell efficiency. The advantage of this device with respect to the hybrid SWCNT-binary CTI lies also in the fact that both ionic liquids and the carbon materials were considered to be stable materials (Fig. 4) and be environmentally friendly. Thus, this kind of composite electrolyte is suitable for application in DSSCs.

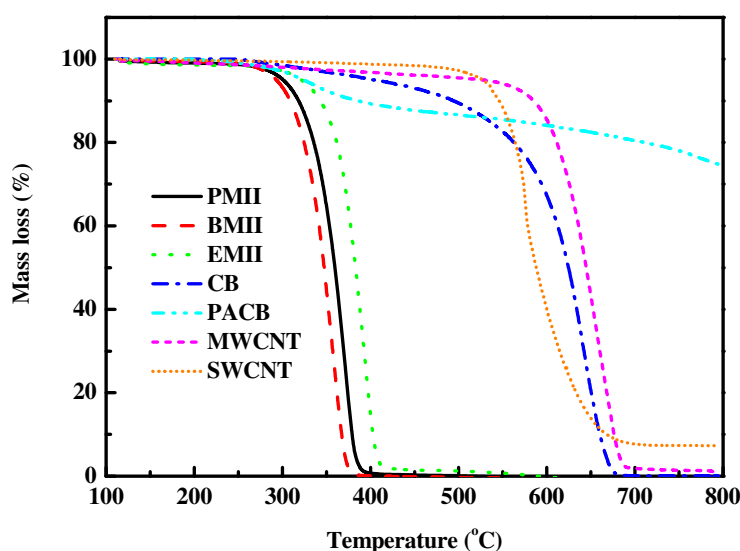


Fig. 4. Thermogravimetric traces of all components in the composite electrolyte (Lee *et al.*, 2010a & 2010b).

### 3. Experimental

#### 3.1 Chemicals and instruments

Both the key chemicals and instruments used for systems A, B, and C are partially listed here. Tert-butyl alcohol (tBA, 96%), 4-tert-butylpyridine (TBP, 99.5%), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF<sub>4</sub>), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF<sub>4</sub>), 1-hexyl-3-methylimidazolium tetrafluoroborate (HMIBF<sub>4</sub>), 1-octyl-3-methylimidazolium tetrafluoroborate (OMIBF<sub>4</sub>), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF<sub>6</sub>), and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMISO<sub>3</sub>CF<sub>3</sub>) were obtained from Acros and used without further purification. The N3 dye, N719 dye and Surlyn® (SX1170-25) spacer were purchased from Solaronix (Solaronix S.A., Aubonne, Switzerland). Lithium iodide (LiI, synthetic grade), iodine (I<sub>2</sub>), poly(ethylene glycol) (PEG, M.W. 20,000), 1-methyl-3-propyl imidazolium iodide (PMII), and 1-butyl-3-methylimidazolium iodide (BMII) were obtained from Merck; 1-ethyl-3-methylimidazolium



iodide (EMII) was obtained from TCI (Tokyo Chemical Industry Co., Ltd.); 1-ethyl-3-methylimidazolium thiocyanate (EMISCN), titanium (IV) isopropoxide (TTIP, 98%), acetonitrile (ACN, 99.99%), acetylacetone (AA, 99.5%), ethanol (99.5%), and isopropyl alcohol (IPA, 99.5%) were obtained from Aldrich. The polyaniline-loaded carbon black (PACB), which was supplied from Sigma-Aldrich Inc., contained 20 wt% of polyaniline emeraldine salt (half oxidized and hydrogenated polyaniline doped with organic sulfonic acid). The single wall carbon nanotubes (SWCNTs, >90%, specific surface area: >300 m<sup>2</sup> g<sup>-1</sup>, diameter: 2nm, length: 5~15 μm) were supplied from Sciencetech Corporation (Taipei, Taiwan). The thermal stability of each component in the composite electrolyte was characterized by a thermogravimetric analyzer (TGA, TGA-7, Perkin-Elmer). The differential scanning calorimetric (DSC, Q20, TA instruments) was used to observe the variations of the binary CTI with various compositions. The morphology of the film was obtained using a field emission scanning electron microscopy (FEI ultra-high resolution FE-SEM with low vacuum mode, Nova NanoSEM 230). The thickness of TiO<sub>2</sub> film was determined using a surface profilometer (Sloan Dektak 3030). The surface of the DSSC was illuminated by a class A quality solar simulator (PEC-L11, AM1.5G, Peccell Technologies, Inc., Japan). The incident light intensity (100 mW cm<sup>-2</sup>) was calibrated with a standard Si cell (PECSI01, Peccell Technologies, Inc.). The photoelectrochemical characteristics of the DSSC were recorded with a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, the Netherlands). EIS data were obtained by the above-mentioned potentiostat/galvanostat equipped with an FRA2 module under a constant light illumination of 100 mW cm<sup>-2</sup>. The frequency range explored was 10 mHz to 65 kHz. The applied bias voltage and ac amplitude were set at the open-circuit voltage of the DSSCs and 10 mV, respectively, between the counter electrode and the FTO-TiO<sub>2</sub>-dye working electrode, starting from the short-circuit condition. The impedance spectra were analyzed by an equivalent circuit model (Han *et al.*, 2004; Han *et al.*, 2006).

### 3.2 Fabrication of DSSCs

The schematic diagram for the fabrication of DSSCs is presented in Fig. 5. The succinct fabrication processes are presented below. A fluorine-doped SnO<sub>2</sub> conducting glass (FTO, 15 Ω sq<sup>-1</sup>, Solaronix S.A., Aubonne, Switzerland) was first cleaned with a neutral cleaner, and then washed with DI-water, acetone, and IPA, sequentially. The conducting surface of the FTO was treated with a solution of TTIP (0.084 g) in ethanol (10 ml) for obtaining a good mechanical contact between the conducting glass and TiO<sub>2</sub> film. A 10 μm-thick film of TiO<sub>2</sub> was coated by doctor blade method onto the treated conducting glass and a portion of 0.4×0.4 cm<sup>2</sup> was selected as the active area by removing the side portions by scraping. The TiO<sub>2</sub> film was gradually heated to 500 °C in an oxygen atmosphere, and subsequently sintered at that temperature for 30 min. After sintering at 500 °C and cooling to 80 °C, the TiO<sub>2</sub> electrode was immersed in a 3×10<sup>-4</sup> M solution of dye (N3 or N719) in ACN and tBA (in the volume ratio of 1:1) at room temperature for 24 h. After dye-adsorption, a 25 μm-thick Surlyn<sup>®</sup> spacer was put on the dye-sensitized TiO<sub>2</sub> electrode and attached by heating. The electrolyte was then coated onto the dye-sensitized TiO<sub>2</sub> film. The dye-sensitized TiO<sub>2</sub> electrode with the electrolyte was assembled with a platinum-sputtered conducting glass electrode (ITO, 7 Ω sq<sup>-1</sup>, Ritek), and the edges were sealed by UV glue (Optocast 3410 40K GEN2, Alexander Jewels Co., LTD.). As for the organic solvent electrolyte, a mixture of 0.1 M LiI, 0.6 M PMII, 0.05 M I<sub>2</sub>, and 0.5 M TBP in gamma-butyrolactone (GBL, Fluka) was used.

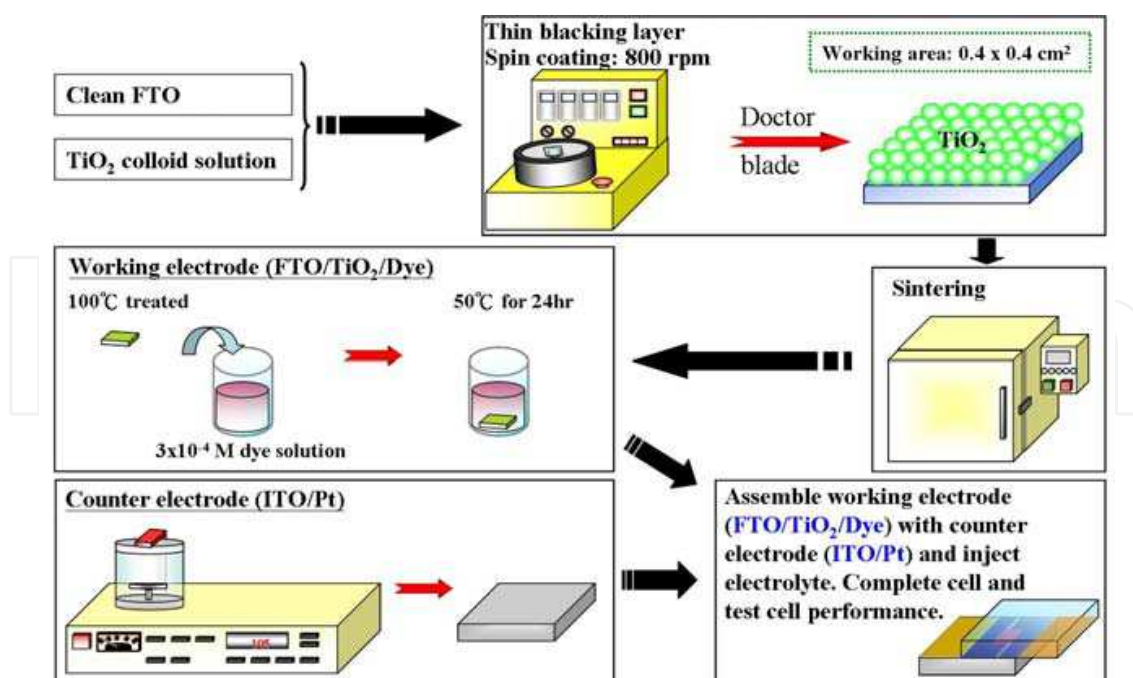


Fig. 5. Schematic diagram for the fabrication processes of DSSCs.

### 3.3 Preparation of quasi-solid-state electrolytes with ILs (system A)

The bi-IL electrolytes are obtained by mixing BMII with EMIBF<sub>4</sub>, BMIBF<sub>4</sub>, HMIBF<sub>4</sub>, OMIBF<sub>4</sub>, BMIPF<sub>6</sub>, or BMISO<sub>3</sub>CF<sub>3</sub> (13:7, v/v), respectively, followed by addition of 0.2 M I<sub>2</sub> and 0.5 M TBP. The prepared electrolytes were injected into the gap between the electrodes by capillarity, and the injecting process was kept at 80 °C because the viscosity of the IL electrolyte at 80 °C was low enough to penetrate into the space.

### 3.4 Preparation of near-solid-state electrolytes with nanoparticles solidified ILs (system B)

The composite electrolyte (Fig. 6) was prepared by mixing a solid powder of PACB or carbon black (CB, Alfa Aesar, 99.9%, *ca.* 42 nm) and one of the ILs mentioned above in a weight ratio of 1:8. Carbon black, owing to its larger size than the pore size of TiO<sub>2</sub> film (about 15-25 nm), is not expected to infiltrate into the film. At the same time, ACN was added to the composite to improve the mixing condition, and the contents were moved to a vacuum oven to obtain a well-mixed composite electrolyte. The composite electrolyte was then coated onto the dye-sensitized TiO<sub>2</sub> film at 80 °C to ensure that the IL can penetrate well into the porous structure.

### 3.5 Preparation of all-solid-state electrolytes with IL crystals (system C)

The hybrid SWCNT-binary CTIs were prepared by mixing the solid powder (SWCNTs) and the binary ILs (PMII and EMII) mentioned above in a weight ratio of 1:9. At the same time, ACN was added to the composite to improve the mixing, and was removed on a hot plate at a temperature of 90 °C. The hybrid SWCNT-binary CTI was then put onto the dye-sensitized TiO<sub>2</sub> film at 90 °C to ensure that the ILs can penetrate well into the porous structure and remove the residual ACN. From Fig. 7a, it shows that EMII and PMII have different colors, namely, bright yellow and deep brown, respectively. With the increase of addition of PMII

into EMII (0 to 80 wt%) the binary CTI (EMII mix with PMII) turns uniformly into brown color. Besides, the binary CTI (EMII/PMII = 40/60) with the addition of SWCNTs still has a solid-like form in an oven at 75 °C (Fig. 7b).



Fig. 6. The photograph of the composite electrolyte prepared with PACB and ILs (Lee *et al.*, 2010a).

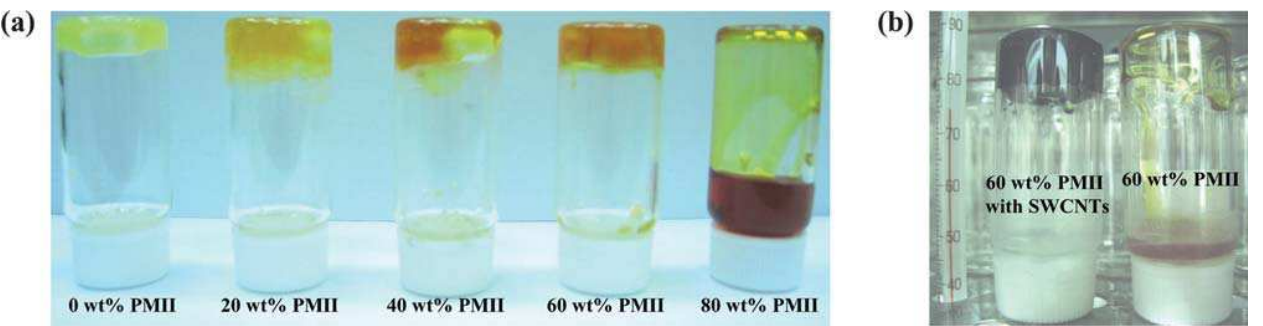


Fig. 7. (a) The pictures of the binary CTI with different weight percents of PMII. (b) The pictures of the binary CTI containing 60 wt% PMII with or without SWCNTs at 75 °C (Lee *et al.*, 2010b).

4. Results and discussions of system A

In system A, steady-state voltammograms for I<sup>-</sup>/I<sub>3</sub><sup>-</sup> in 1-alkyl-3-methylimidazolium tetrafluoroborate with various lengths of side chain (C=2, 4, 6, 8) and BMI<sup>+</sup> with different anions are performed and the calculated apparent diffusivity (*D<sub>app</sub>*) are shown in Table 1.

ILs	<i>D<sub>app</sub></i> (I <sup>-</sup> ) (cm <sup>2</sup> s <sup>-1</sup> )	<i>D<sub>app</sub></i> (I <sub>3</sub> <sup>-</sup> ) (cm <sup>2</sup> s <sup>-1</sup> )	<i>J<sub>sc</sub></i> (mA cm <sup>-2</sup> )	<i>V<sub>oc</sub></i> (V)	<i>η</i> (%)	<i>FF</i>	<i>R<sub>diff</sub></i> (ohm)	<i>τ<sub>n</sub></i> (ms) <sup>a</sup>
EMIBF <sub>4</sub>	4.40×10 <sup>-7</sup>	2.01×10 <sup>-7</sup>	7.78	0.647	2.98	0.60	45.2	12.3
BMIBF <sub>4</sub>	3.64×10 <sup>-7</sup>	1.36×10 <sup>-7</sup>	7.77	0.651	3.02	0.59	58.1	12.5
HMIBF <sub>4</sub>	2.98×10 <sup>-7</sup>	1.04×10 <sup>-7</sup>	7.51	0.643	2.81	0.58	63.4	14.4
OMIBF <sub>4</sub>	2.71×10 <sup>-7</sup>	1.02×10 <sup>-7</sup>	7.46	0.651	2.57	0.53	70.3	22.9
BMIPF <sub>6</sub>	3.18×10 <sup>-7</sup>	1.20×10 <sup>-7</sup>	6.76	0.649	2.61	0.60	60.2	12.7
BMISO <sub>3</sub> CF <sub>3</sub>	3.58×10 <sup>-7</sup>	1.31×10 <sup>-7</sup>	10.18	0.657	4.11	0.62	57.5	20.1

<sup>a</sup> The values of *τ<sub>n</sub>* were calculated from the fitting data of EIS measurements.

Table 1. The photovoltaic and EIS parameters of the DSSCs based on bi-ionic liquids with various side chain lengths and anions. The ionic diffusion coefficients were calculated from the limiting currents measured by a 10 μm radius Pt ultramicroelectrode (Lee *et al.*, 2009b).

The result shows that the  $D_{app}$  of  $I^-$  and  $I_3^-$  decrease from  $4.40 \times 10^{-7}$  to  $2.71 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  and  $2.01 \times 10^{-7}$  to  $1.02 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , respectively, by increasing the side chain length of ILs from C2 to C8. On the other hand,  $BMI^+$  containing  $BF_4^-$  has higher  $D_{app}$  than  $PF_6^-$  or  $SO_3CF_3^-$ . The  $D_{app}$  results show an inverse trend to the viscosity of the ILs. The photovoltaic characteristic parameters of DSSCs based on different ILs are also listed in Table 1. The DSSC containing

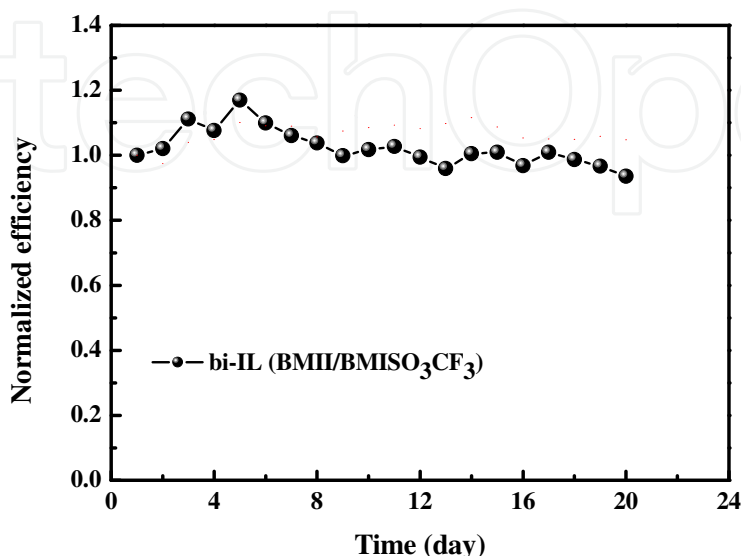


Fig. 8. The durability tests of the DSSCs based on bi-ILs (BMII/BMISO<sub>3</sub>CF<sub>3</sub>) (Lee *et al.*, 2010b).

EMIBF<sub>4</sub> has higher current density and conversion efficiency than other chain lengths due to higher  $D_{app}$  of  $I^-$  and  $I_3^-$ . The charge transport in DSSCs was determined by the transport of  $I^-/I_3^-$  in the IL electrolytes, thus the decreased fill factor ( $FF$ ) and cell conversion efficiency with the increase of the side chain length of IL is resulted from the increased viscosity for longer chain length. The equivalent circuit employed for the curves fitted the impedance spectra of the DSSCs are also shown in Table 1. The  $R_{diff}$  increased with the increase in the side chain length, and the similar trend has been observed with the  $D_{app}$  also. Meanwhile, the time constant ( $\tau_n$ ) of electron in TiO<sub>2</sub> film increases from 12.3 to 22.9 ms with the increase in side chain length from C2 to C8. This result is similar to the previously reported results by Kubo *et al.* (Kubo *et al.*, 2002), where the electron lifetimes increase with increasing of side chain length of imidazolium iodides from C3 to C9. Thus, it was found that the DSSC containing C7-imidazolium iodides has the best conversion efficiency due to the combination effects of the electron lifetime in TiO<sub>2</sub> electrode and the electrolyte viscosity (Kubo *et al.*, 2002). In our system, as listed in Table 1, the DSSC containing EMIBF<sub>4</sub> has higher current density than other longer side chain lengths. Meanwhile, the  $FF$  significantly decreased with the increase in side chain length, which was due to the increase in ions diffusion resistance and the lower electron transfer at the counter electrode. It is supported via the high-frequency (103-105 Hz) peaks in the Bode phase plot, shifting to lower frequency with increasing of side chain length (not shown here). Consequently, the electron lifetime in TiO<sub>2</sub> electrode and the viscosity of electrolyte are the two main factors on the cell performances of DSSCs with bi-IL electrolyte systems. As to the effect of anions of ionic liquids on DSSCs, the time constants of the BMIBF<sub>4</sub>, BMIPF<sub>6</sub> and BMISO<sub>3</sub>CF<sub>3</sub> based DSSCs are found to be 12.5, 12.7 and 20.1 ms, respectively, as shown in Table 1. Thus, the DSSC



containing BMISO<sub>3</sub>CF<sub>3</sub> has longer electron lifetime, which resulted in the best cell performance, in which the short-circuit current density (*J*<sub>sc</sub>), open-circuit voltage (*V*<sub>oc</sub>), conversion efficiency (*η*) and *FF* were 10.18 mA cm<sup>-2</sup>, 0.657 V, 4.11% and 0.62, respectively, as listed in Table 1. As shown in Fig. 8, the at-rest long-term stability of DSSCs with BMISO<sub>3</sub>CF<sub>3</sub> gives slight decay (smaller than 5%) after being stored for more than 576 h.

References	Composition	Dye	<i>η</i> (%)	Stability
Wang <i>et al.</i> , 2003b	Binary ILs (PMII/EMIDCN) with I <sup>-</sup> /I <sub>3</sub> <sup>-</sup>	Z907	6.60	N/A
Wang <i>et al.</i> , 2004a	Binary ILs (PMII/EMINSC) with I <sup>-</sup> /I <sub>3</sub> <sup>-</sup>	Z907	7.00	N/A
Wang <i>et al.</i> , 2004b	IL with SeCN <sup>-</sup> /(SeCN) <sub>3</sub> <sup>-</sup> , Iodine-free	Z907	7.50	N/A
Kuang <i>et al.</i> , 2004b	Binary ILs (PMII/EMIB(CN) <sub>4</sub> ) with I <sup>-</sup> /I <sub>3</sub> <sup>-</sup>	K77	7.60	1,000 h light-soaking at 60 °C, decay 9%
Jhong <i>et al.</i> , 2009	Binary ILs (PMII/G.Cl) with I <sup>-</sup> /I <sub>3</sub> <sup>-</sup>	D149	3.88	N/A
Lee <i>et al.</i> , 2009b (system A)	Binary ILs (BMII/BMISO <sub>3</sub> CF <sub>3</sub> ) with I <sup>-</sup> /I <sub>3</sub> <sup>-</sup>	N3	4.11	576 h at-rest at 25 °C, decay < 5%

Table 2. Partial literatures reported on the quasi-solid-state DSSCs with ILs electrolytes.

Table 2 is a partial list of the quasi-solid-state DSSCs reported in literatures based on IL electrolytes. Normally, the conversion efficiency obtained with ILs at full solar irradiation (AM 1.5, 100 mW cm<sup>-2</sup>) have been markedly lower than those achieved with organic solvent based electrolytes, only recently efficiencies of 5~6% were achieved for DSSCs with pure ILs electrolyte (Wang *et al.*, 2002; Wang *et al.*, 2003a). Wang *et al.* (Wang *et al.*, 2003b) first prepared an binary-ILs electrolyte that consisted of PMII, EMIDCN, and LiI in a device to obtain a cell with an efficiency of 6.6% at full solar irradiation. However, their subsequent research showed that the presence of EMIDCN in the bi-ILs electrolyte led to an instability of the cells under visible light soaking. Hence, they used a new ILs electrolyte composed of PMII and EMINCS and a cell efficiency of 7.00% was obtained (Wang *et al.*, 2004a). In addition, they also developed an iodine-free SeCN<sup>-</sup>/(SeCN)<sub>3</sub><sup>-</sup> based IL electrolyte by incorporation of a new, low viscosity IL EMISecN, and a high efficiency of 7.5% was achieved (Wang *et al.*, 2004b). For the first time an alternative redox couple has been identified that can rival or even exceed the performance of the iodide/triiodide couple at full sunlight. Kuang *et al.* reported on a new record of 7.6% cell efficiency under full sunlight irradiation using a EMIB(CN)<sub>4</sub> based binary-ILs electrolyte in combination with the high-molar-extinction-coefficient sensitizer K77 (Kuang *et al.*, 2004b). The cell with EMIB(CN)<sub>4</sub> based binary-ILs electrolyte maintained more than 90% of their initial efficiency under light-soaking at 60 °C for 1000 h. Jhong *et al.* utilized a quaternary ammonium salt-derivative IL, called G. Cl, which is a eutectic mixture of glycerol and choline iodide as electrolyte for DSSCs, and a cell efficiency of 3.88% was achieved (Jhong *et al.*, 2009).



5. Results and discussions of system B

In system B, two ILs, BMII and PMII with different viscosities, were used as charge carrier mediators of the DSSCs. Table 3 (Case 2) shows that the cell efficiency of PMII/CB device is 4.38% ( $J_{SC}$ : 8.89 mA cm<sup>-2</sup>,  $V_{OC}$ : 726 mV,  $FF$ : 0.68), which is higher than that of BMII/CB device with an efficiency of 3.68% ( $J_{SC}$ : 8.04 mA cm<sup>-2</sup>,  $V_{OC}$ : 724 mV,  $FF$ : 0.63). As shown in Fig. 9a, PMII/CB cell has smaller  $R_{ct2}$  than BMII/CB cell, because PMII has lower viscosity than BMII (Pringle *et al.*, 2002; Fredlake *et al.*, 2004). In order to study the role of CB, ILs/CB composite electrolytes were replaced with the corresponding two bare ILs, i.e., with BMII and PMII. It can be seen in Table 3 (Case 1) that the cell efficiencies in both cases are much smaller than 1%, due to significant decrease in both  $J_{SC}$  and  $FF$ . Through the EIS analysis for pure ILs (Fig. 9b), the Warburg diffusion resistances ( $R_{diff}$ ) for I<sup>-</sup> and I<sub>3</sub><sup>-</sup> ions and the resistances of the charge-transfer at the counter electrodes ( $R_{ct1}$ ) have increased by about 2.5 and 5 times, respectively, as compared to the corresponding values from Fig. 9a. From these observations, it is more clear that the presence of CB as the extended electron transfer material (EETM) facilitates the electron transfer from the counter electrode to I<sub>3</sub><sup>-</sup> ions; a shorter length for I<sub>3</sub><sup>-</sup> ions and thereby for I<sup>-</sup> ions is created which enables the redox couple to work more efficiently than they would in the absence of the carbon material. From the literature reported by Ikeda *et al.* (Ikeda *et al.*, 2006), we found that the incorporation of I<sub>2</sub> is not necessary as shown in Table 4, and even detrimental in our case (Lee *et al.*, 2010a). This suggests that the iodide anion based IL can provide sufficient I<sup>-</sup> for the regeneration of the oxidized dye under illumination; I<sup>-</sup> in turn oxidizes to I<sub>3</sub><sup>-</sup>, which can be reduced back to I<sup>-</sup> at the EETM. Increasing the content of I<sub>2</sub> can increase concentration of polyiodides in the porous dye-coated TiO<sub>2</sub> matrix. It can facilitate recombination of injected conduction band electrons with polyiodides, and increase the dark current (Lee *et al.*, 2010a). Furthermore, increasing I<sub>2</sub> content also leads to enhanced light absorption even in the visible range by the carrier mediator existing in the porous dye-coated TiO<sub>2</sub> matrix. This decreases the light-harvesting of dye molecules (Wang *et al.*, 2006). Therefore, both  $V_{OC}$  and  $J_{SC}$  show decreases with the increases in the wt% of I<sub>2</sub> for this system. When CB was replaced with PACB, the highest cell efficiency of 5.81% was obtained. The results are shown in Table 3 (Case 3). A smaller interfacial resistance was obtained for the DSSC with PMII/PACB composite electrolyte than that for the cell with PMII/CB (Lee *et al.*, 2010a). According to a recent

Electrolyte	$V_{OC}$ (mV)	$J_{SC}$ (mA cm <sup>-2</sup> )	$\eta$ (%)	$FF$
Case 1 (Bare ILs)				
BMII	740	1.10	0.3	0.37
PMII	726	2.17	0.6	0.38
Case 2 (ILs/CB composite electrolytes)				
BMII/CB	724	8.04	3.68	0.63
PMII/CB	726	8.89	4.38	0.68
Case 3 (PMII/PACB composite electrolyte)				
PMII/PACB	737	12.20	5.81	0.65

Table 3. Photovoltaic parameters of the DSSCs with different composite electrolytes and with bare IL electrolytes, measured at 100 mWcm<sup>-2</sup> light intensity (Lee *et al.*, 2010a).

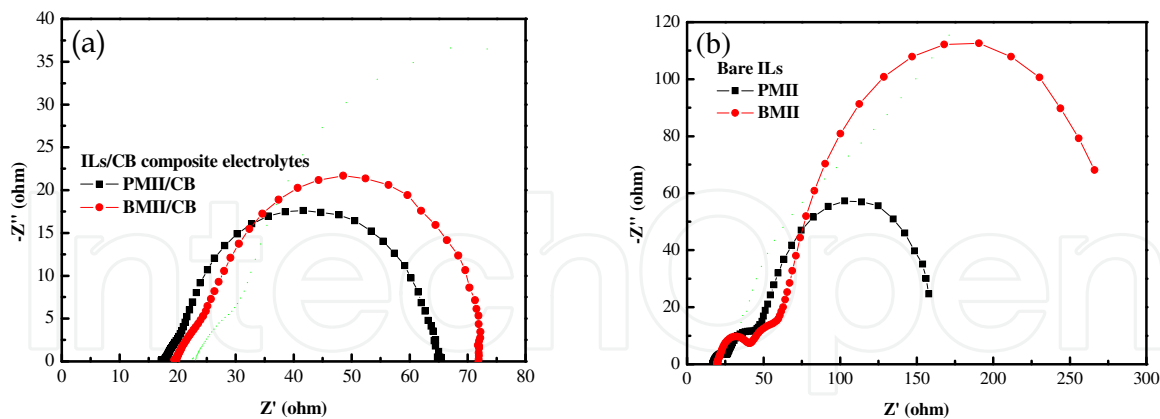


Fig. 9. EIS of the DSSCs with (a) PMII/CB and BMII/CB electrolytes (b) pure IL electrolytes, measured at 100 mW cm<sup>-2</sup> light intensity under open-circuit voltage (Lee *et al.*, 2010a).

Iodine content (%)	$J_{SC}$ (mA cm <sup>-2</sup> )	$V_{OC}$ (V)	$FF$	$\eta$ (%)
0	12.8	0.58	0.47	3.48
1.2	10.0	0.55	0.48	2.76
2.4	9.99	0.53	0.50	2.68
3.6	8.79	0.52	0.53	2.47
14	6.88	0.50	0.55	1.87

Table 4. Photoelectric performances of dye-TiO<sub>2</sub>/PACB-EOI/FTO solid-state dye-sensitized photocells measured under simulated solar irradiation of 1 sun (AM1.5) and influence of the content of I<sub>2</sub> (wt%) added in the PACB-EOI layer on the cell performance (Ikeda *et al.*, 2006).

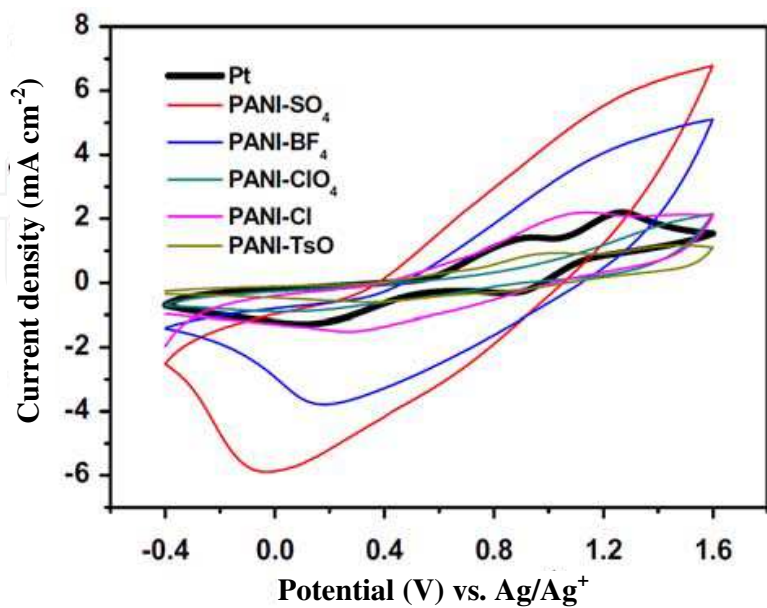


Fig. 10. CVs of electropolymerized-PANI with 400 mC cm<sup>-2</sup> doped by different counterions and Pt CEs in 10 mM LiI, 1 mM I<sub>2</sub>, and 0.1 M LiClO<sub>4</sub> acetonitrile solution (Li *et al.*, 2009).

report by Li (Li *et al.*, 2009), polyaniline shows high reduction current for the reduction of  $I_3^-$  (Fig. 10). Based on this report, it is inferred that more charge-transfer paths were formed between PMII and the polymer chains of PACB than those between the PMII and bare CB. This can be the reason for the better performance of the cell with PACB than that with CB. Interestingly, the devices using bare ITO as counter electrode still exhibit cell efficiencies of 3.65% and 2.67% for PMII/PACB and PMII/CB, respectively (Lee *et al.*, 2010a). Therefore, the significance of these carbon materials (PACB or CB) as catalysts in the form of EETM for the reduction of  $I_3^-$  ions to  $I^-$  ions at the counter electrode was univocally established from the fact that an efficiency as high as 3.65% could be achieved for the DSSC using bare ITO glass as the counter electrode. Thus it is established through the above observations that the carbon material in the composite electrolyte serves simultaneously as a charge transporter in the electrolyte and as a catalyst for electrochemical reduction of  $I_3^-$  ions. To increase the efficiency further, the low-viscosity IL, EMISCN (25 cP at 21°C), was added into PMII (900 cP at 20 °C) to form a binary ionic liquid (bi-IL). With a volume ratio of 35/65 for EMISCN/PMII, a cell efficiency of 6.15% was achieved, indicating the beneficial effect of EMISCN (Chen *et al.*, 2010). The enhancement in the efficiency of the DSSC with EMISCN, with reference to the efficiency of the best cell without this IL (5.81%) is attributed to the less viscous nature of the EMISCN, which provides better penetration of the composite electrolyte into  $TiO_2$  and also better conductivity of the electrolyte for  $I^-$  and  $I_3^-$  ions. Figure 11 shows the durability of the cell with the PACB-bi-IL composite electrolyte at 70 °C. The DSSC with the PACB-bi-IL composite electrolyte shows an extraordinary durability even at 70 °C. The cell with organic liquid electrolyte lost its efficiency virtually in no time. Thus, these results proved beyond doubt that the durability of the DSSC with PACB-bi-IL composite electrolyte is far superior to that of a cell with organic liquid electrolyte.

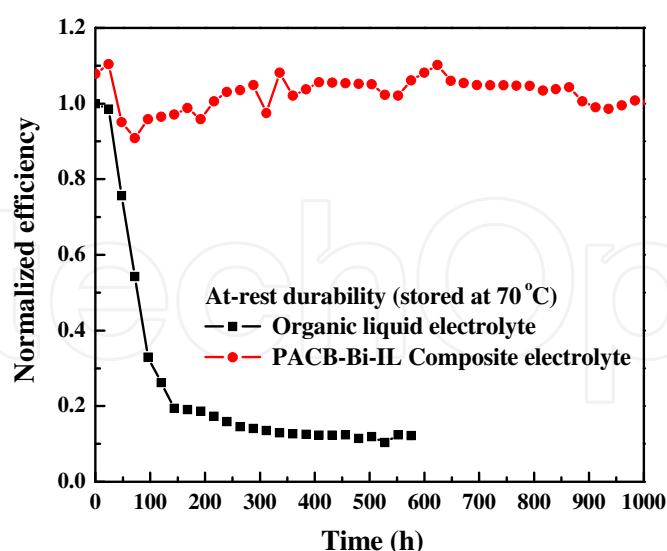


Fig. 11. At-rest durabilities of DSSCs stored at 70 °C, one with PACB-bi-IL composite electrolyte and the other with an organic liquid electrolyte (Chen *et al.*, 2010).

Table 5 is a partial list of the near-solid-state DSSCs reported in literatures with nanoparticles solidified ILs electrolytes. Hsui *et al.* prepared ionic gel electrolytes by

dispersing carbon materials (MWCNT, SWCNT, carbon black, carbon fiber and graphite) and TiO<sub>2</sub> nanoparticles into binary ILs electrolytes for DSSCs and obtained the best cell efficiency of 5.00% when the TiO<sub>2</sub> nanoparticles were incorporated (Hsui *et al.*, 2004). Ikeda *et al.* investigated a clay-like conductive composite electrolyte comprising polyaniline-loaded carbon black particles and an ethyleneoxide-substituted imidazolium iodide as shown in Fig. 12. The composite electrolyte was sandwiched between dye-sensitized porous TiO<sub>2</sub> and counter electrode to form a near-solid-state DSSC, which achieved a cell efficiency of 3.48% at full sunlight irradiation without the addition of iodine (Ikeda *et al.*, 2006). Katakabe *et al.* demonstrated that the exchange-reaction-based diffusion and the interfacial charge-transfer rates of an iodide/triiodide redox couple in an ionic liquid were enhanced by the addition of SiO<sub>2</sub> nanoparticles, although the composites successively became gels and solids with increasing nanoparticle content. Because of this acceleration of the charge transport and the interfacial charge-transfer rates, dye-sensitized solar cells using the

References	Composition	Dye	$\eta$ (%)	Stability
Hsui <i>et al.</i> , 2004	Binary ILs (EMII/EMITFSI) with I <sup>-</sup> /I <sub>3</sub> <sup>-</sup> , Addition of TiO <sub>2</sub>	N3	5.00	N/A
Ikeda <i>et al.</i> , 2006	EOI with SWCNTs, Iodine-free	N719	3.48	N/A
Katakabe <i>et al.</i> , 2007	Binary ILs (EMII/G.Cl) with I <sup>-</sup> /I <sub>3</sub> <sup>-</sup> , Addition of SiO <sub>2</sub>	N719	3.70	N/A
Chen <i>et al.</i> , 2010 (system B)	Binary ILs (PMII/EMISCN) with I <sup>-</sup> /I <sub>3</sub> <sup>-</sup> , Iodine-free	N719	6.15	1,000 h at-rest at 70 °C, no dacay

Table 5. Partial literatures reported on the near-solid-state DSSCs with nanoparticles solidified ILs electrolytes.

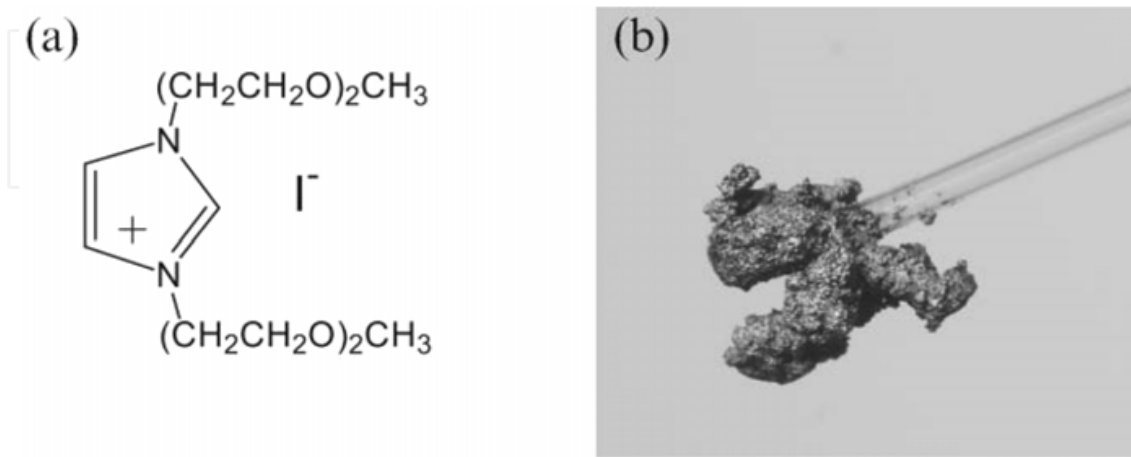


Fig. 12. (a) Molecular structure of the ethylene oxide-type ionic liquid iodide, EOI; (b) clay-like highly viscous, black paste of polyaniline-carbon black (PACB)-EOI composite (Ikeda *et al.*, 2006).

composite electrolytes achieved high conversion efficiencies of 3.70%, comparable to those using the pure or neat ionic liquid electrolyte (Katakabe *et al.*, 2007). In system B (Chen *et al.*, 2010), the near-solid-state DSSC with a non-volatile composite electrolyte, comprising PACB and the ionic liquid, PMII, without adding iodine showed a power conversion efficiency of 5.81%. A higher efficiency of 6.15% was achieved with the same composite electrolyte with the addition of EMISCN, the highest for any iodine-free quasi-solid-state DSSC. Besides, system B showed an unfailing stability at 70 °C, while the cell with liquid electrolyte lost its performance almost immediately. Thus, an iodine-free, cost-effective, efficient, and durable quasi-solid-state DSSC was realized.

6. Results and discussions of system C

Table 6 shows the photovoltaic parameters of the DSSCs using EMII as CTI with or without the incorporation of SWCNTs. A higher efficiency (1.88%) all-solid-state DSSC with this hybrid SWCNT-EMII was obtained as compared to that containing a bare EMII (0.41%). From EIS analysis, hybrid SWCNT-EMII cell has both smaller  $R_{ct2}$  and  $R_{diff}$  than those of a bare EMII cell. From this analysis, it is clear that the presence of SWCNTs as the EETM facilitates electron transfer from the counter electrode to  $I_3^-$  ions; a shorter diffusion length for  $I_3^-$  ions and thereby for  $I^-$  ions created, which enables the redox couple to work more efficiently than they would in the absence of SWCNTs. Moreover, it was found that incorporation of  $I_2$  is not necessary to drive the device. To further improve the cell efficiency, PMII was used; PMII acts simultaneously as CTI and a crystal growth inhibitor. Besides, the binary CTI exhibits a solid-like form when the content of PMII is increased to a weight percent of 60%, and a smoother surface morphology of the binary CTI is observed in this case as compared to that without the addition of PMII (Fig. 13). It is known that ionic crystallization would prevent the filling of solid-state electrolyte into the  $TiO_2$  porous structure and result in a decrease in photoelectrochemical responses of the device. Therefore, the inhibition of the crystal growth is expected to improve the cell performance for the all- solid-state DSSCs (Kumara *et al.*, 2002; Perera *et al.*, 2003). From DSC scans (Fig. 14), the melting point ( $T_m$ ) of the binary CTI decreases with the increase in the content of PMII. At a 60 weight percent of PMII, the melting point reaches 35 °C, which is already close to the room temperature. Table 7 shows that the cell efficiency increases with the increase in the content of PMII, and a cell efficiency of 3.49% was achieved at a weight ratio of 40/60 (EMII/PMII). From the EIS analysis, smaller  $R_{ct2}$  and  $R_{diff}$  are observed for the all-solid-state DSSCs containing hybrid SWCNT-binary CTI, as compared to the case without adding PMII; in consistency with our explanation that the presence of PMII leads to less

CTI layer	$J_{SC}$ (mA cm <sup>-2</sup> )	$V_{OC}$ (mV)	$\eta$ (%)	$FF$	$R_{ct2}$ (ohm)	$R_{diff}$ (ohm)
Bare EMII	1.11	652	0.41	0.56	685	-
SWCNTs-EMII	5.09	680	1.88	0.54	121	371

Table 6. The photovoltaic parameters of the DSSCs using EMII as CTI with or without the incorporation of SWCNTs (Lee *et al.*, 2010b).



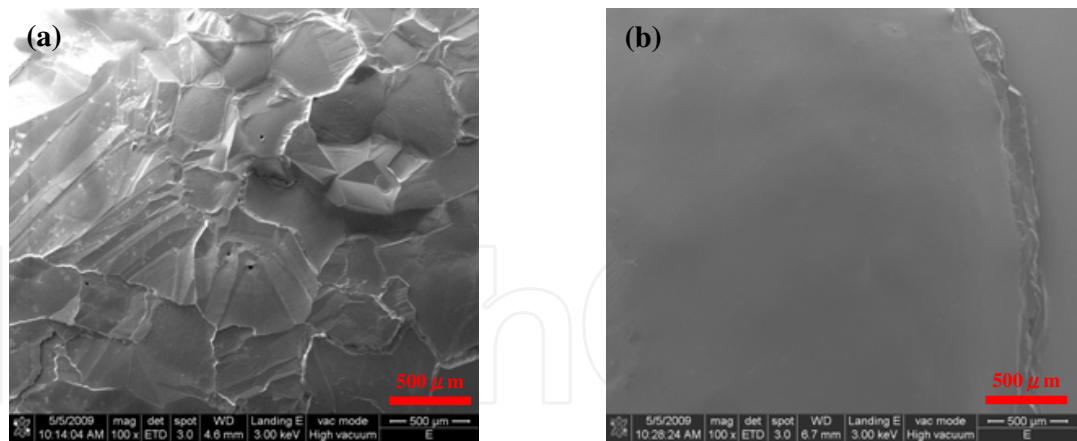


Fig. 13. SEM images of (a) bare EMII and (b) co-CTI, both after recrystallization by treating at 90 °C; EMII/PMII: 40/60 (weight ratio) (Lee *et al.*, 2010b).

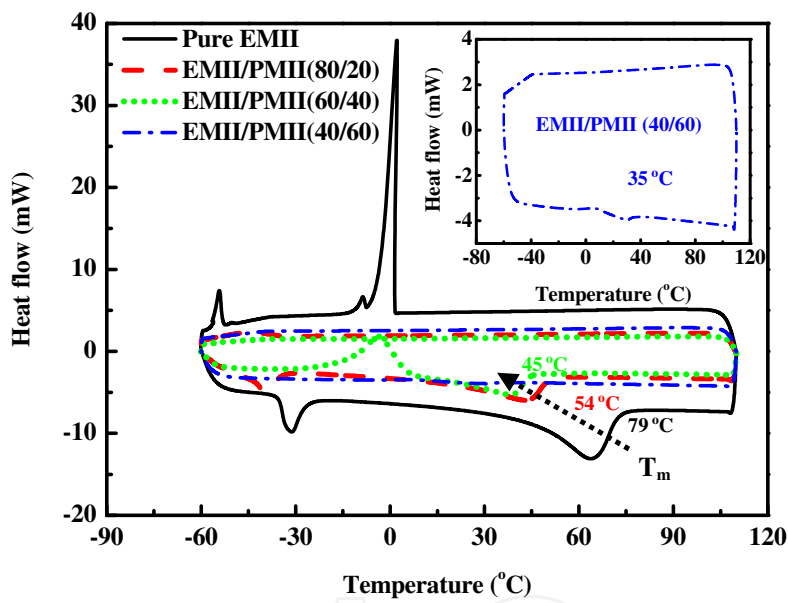


Fig. 14. DSC traces of binary CTI with different weight percents of PMII. The inset shows the magnified picture of the binary CTI with 60 wt% PMII (Lee *et al.*, 2010b).

EMII/PMII	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (mV)	$\eta$ (%)	$FF$	$R_{ct2}$ (ohm)	$R_{diff}$ (ohm)
100 : 0	5.09	680	1.88	0.54	121	371
80 : 20	5.32	706	2.23	0.59	81	167
60 : 40	6.70	716	3.01	0.62	75	84
40 : 60	8.07	716	3.49	0.61	59	68

Table 7. Photovoltaic performance parameters of the DSSCs with hybrid SWCNT-EMII, incorporating various amounts of PMII (wt%), measured at 100 mW cm<sup>-2</sup> (Lee *et al.*, 2010b).

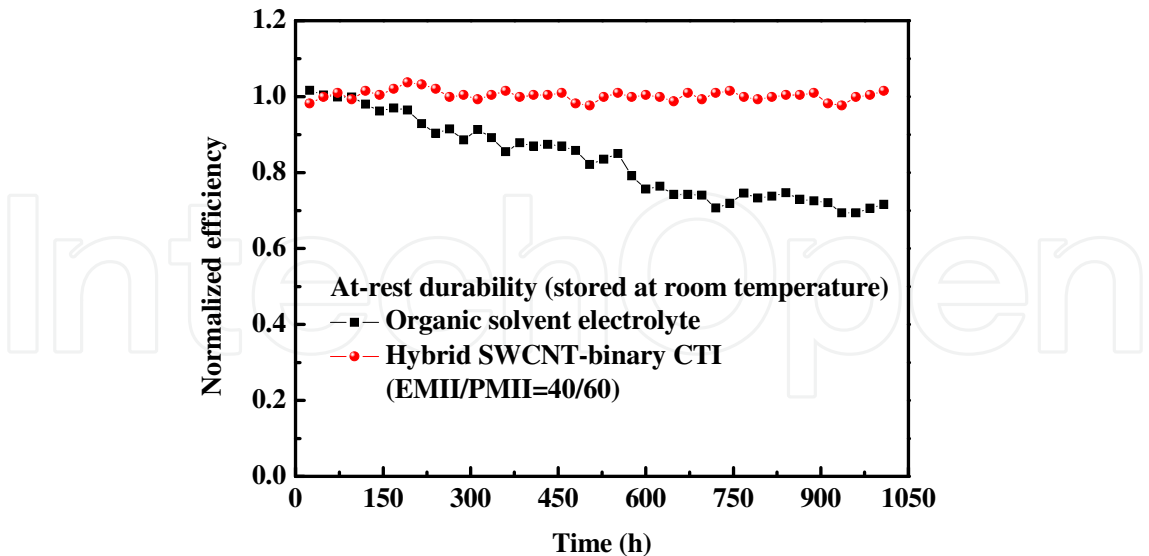


Fig. 15. The normalized efficiencies of DSSCs based on both hybrid SWCNT-binary CTI (EMII/PMII=40/60) and organic solvent electrolyte, respectively (Lee *et al.*, 2010b).

crystallization nature of the binary CTI, which penetrates deeper into the TiO<sub>2</sub> and enhances the cell performance. Figure 15 shows the at-rest durability data of the DSSCs with hybrid SWCNT-binary CTI and organic liquid electrolyte. The proposed all-solid-state DSSCs showed excellent durability when compared with that of the cell with organic liquid electrolyte. It is noticed that the overall cell efficiency of the solid-state DSSC has increased about 1.5%, the overall cell efficiency of the DSSC with organic liquid electrolyte has decreased about 30% after more than 1,000 h, despite the fact that the boiling point of the organic solvent, GBL is 204 °C.

Table 8 is a partial list of the all-solid-state DSSCs obtained from the literatures. Ikeda *et al.* (Ikeda *et al.*, 2005) constructed an all-solid-state DSSC with a poly(N-vinyl-carbazole) (PVK) hole transporter mediated by an alkali iodide as illustrated in Fig. 16. They reached a cell efficiency of 2.0% under one sun irradiation, but without the incorporation of volatile

References	Composition	Dye	$\eta$ (%)	Stability
Ikeda <i>et al.</i> , 2005	PVK/alkali iodide/graphite with I <sup>-</sup> /I <sub>3</sub> <sup>-</sup> , Iodine-free	N719	2.00	N/A
Zhao <i>et al.</i> , 2008	IL crystal (MH-II) with I <sup>-</sup> /I <sub>3</sub> <sup>-</sup> and MPBF <sub>4</sub>	N3	3.10	30 days at-rest at 25 °C, decay 40%
Midya <i>et al.</i> , 2010	IL crystal (SD) with I <sup>-</sup> /I <sub>3</sub> <sup>-</sup> and EMIB(CN) <sub>4</sub>	N719	2.85	N/A
Lee <i>et al.</i> , 2010b (system C)	IL crystal (EMII) with SWCNT and PMII, Iodine-free	N719	3.49	1,000 h at-rest at 25 °C, no decay

Table 8. Partial literatures reported on the all-solid-state DSSCs.

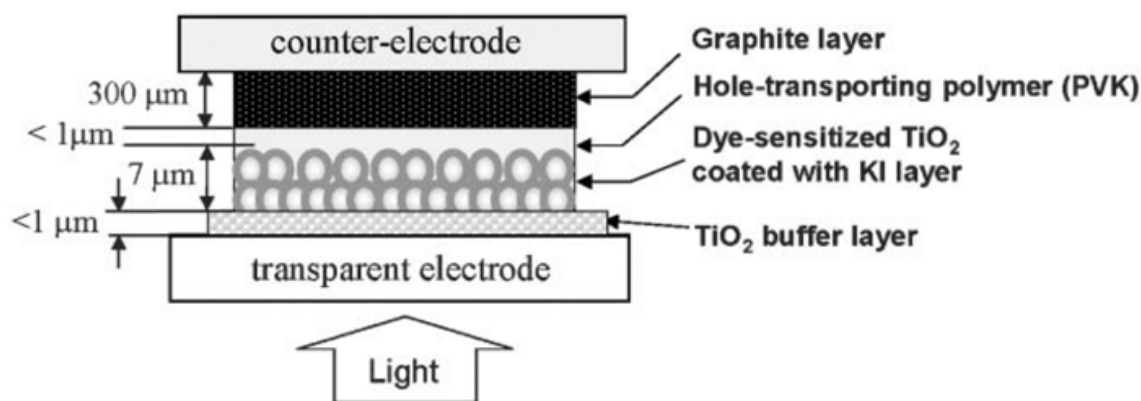


Fig. 16. Schematic structure of a solid-state dye-sensitized solar cell using PVK as a hole-transporting layer. (Ikeda *et al.*, 2005).

components (TBP, I<sub>2</sub>) in their devices. Zhao *et al.* (Zhao *et al.*, 2008) reported a solid-state DSSC utilizing imidazolium-type ionic crystal as transfer layer, and obtained a good cell efficiency of 3.1% under one sun irradiation by adopting 1-methyl-3-propylimidazolium tetra-fluoroborate as a crystal growth inhibitor, lithium bis-trifluoromethanesulfonylimide as a charge transport enhancer, and 4-tert-butylpyridine (TBP) as a carrier recombination inhibitor. As shown in their work (Fig. 17), the cell efficiency remained 60% of the initial value after 30 days at room temperature. Besides, a new class of solid-state ionic conductor based on a carbazole-imidazolium cation structure (Fig. 18) was synthesized by Midya *et al.* and investigated for application in all-solid-state DSSCs (Midya *et al.*, 2010). This kind of solid-state electrolyte containing the designed solid-state ionic conductor and iodine provide dual channels for hole/triiodide transportation (Fig. 19),

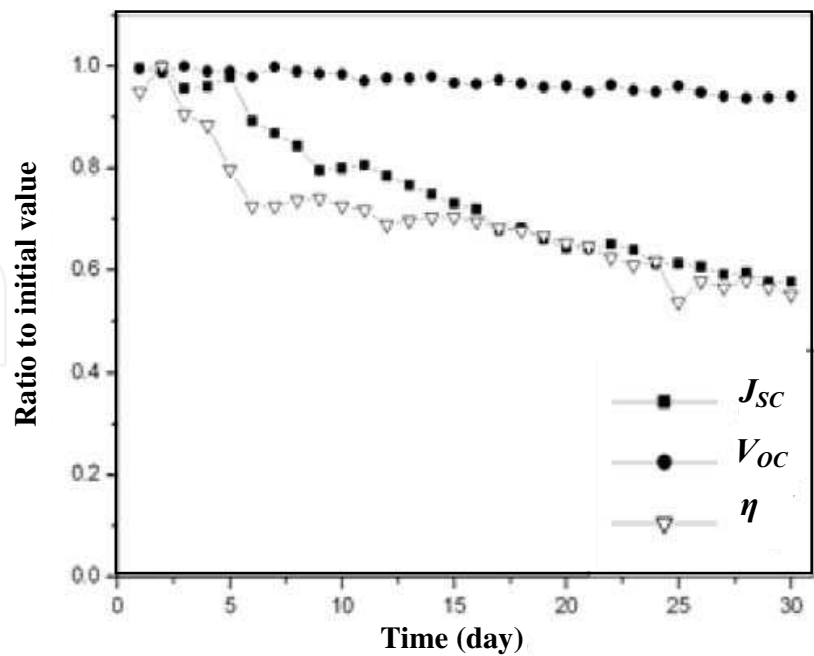


Fig. 17. The stability data of  $V_{OC}$  (●),  $J_{sc}$  (■),  $\eta$  (▽) for an all-solid-state DSSC (Zhao *et al.*, 2008).

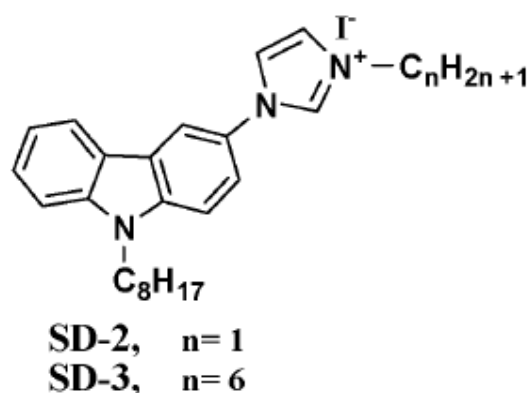


Fig. 18. The molecular structure of solid-state ionic conductor (Midya *et al.*, 2010).

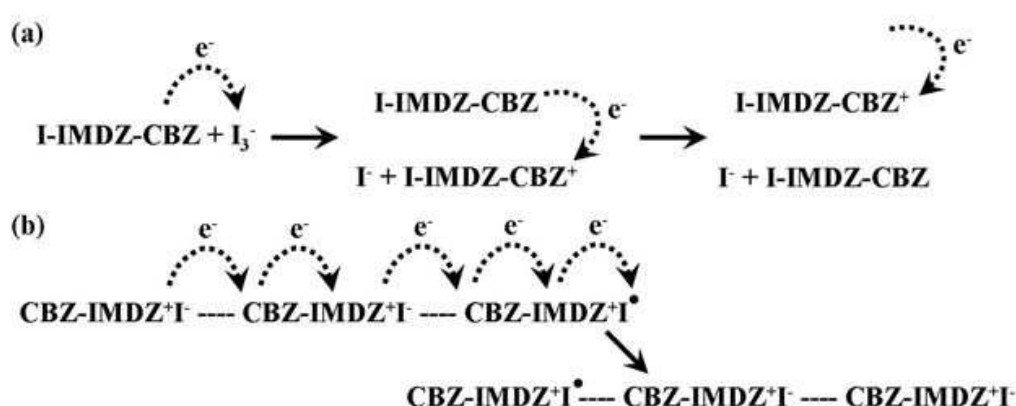


Fig. 19. Schematic illustration of the mechanisms of (a) hole hopping and (b) iodine radical transport through CBZ-IMDZ-I solid-state ionic conductors (Midya *et al.*, 2010).

giving rise to a conversion efficiency of 2.85% under one sun irradiation. System C proved that the all-solid-state DSSC with a hybrid SWCNT-binary CTI should avoid the problem of leakage or evaporation for traditional DSSCs and also provide the useful technique for fabrication of the DSSCs without losing their intrinsic performances. Most importantly, this system provides a unique approach to prepare all-solid-state CTI with organic ionic salts having relatively lower melting points ( $<100\text{ }^{\circ}\text{C}$ ) in contrast to inorganic ionic salts mentioned in literature (Ikeda *et al.*, 2005), which normally having melting points higher than *ca.*  $300\text{ }^{\circ}\text{C}$ . This approach in system C has advantage in that CTI can be filled in the porous  $\text{TiO}_2$  matrix under relatively low heating temperature (says,  $90\text{ }^{\circ}\text{C}$ ). Another novel concept is also introduced, i.e., the melting point of the CTI is controlled through the adjustment of the composition of the binary CTI; this precludes a molecular design for organic ionic salts (Zhao *et al.*, 2008). At the same time, the charge transport is enhanced and both the carrier recombination and the crystallization of CTI is reduced through the incorporation of hybrid SWCNT-binary CTI, and without the incorporation of any volatile component (TBP, iodine etc). The all-solid-state DSSC in this system shows one of the best cell efficiencies, considering those reported in the literatures (Ikeda *et al.*, 2005; Zhao *et al.*, 2008).

## 7. Conclusions and future works

In this chapter, we first review general progress on IL-based electrolytes for DSSCs. The selected researches cover IL electrolytes for DSSCs published during 2002~2010. Efficiencies of 5~6% were initially achieved for DSSCs with pure ILs electrolyte proposed by Wang *et al.* (Wang *et al.*, 2002; Wang *et al.*, 2003a). They (Wang *et al.*, 2003b) firstly prepared a binary-ILs electrolyte (PMII/EMIDCN) and obtained a cell with an improved efficiency of 6.6%. They also used new binary-ILs electrolyte composed of PMII and EMINCS and a cell efficiency of 7.00% was obtained (Wang *et al.*, 2004a). Further, they developed an iodine-free SeCN<sup>-</sup>/(SeCN)<sub>3</sub><sup>-</sup> based IL electrolyte by incorporation of a new, low viscosity IL EMISCN, and a high efficiency of 7.5% was achieved (Wang *et al.*, 2004b) for the first time. Kuang *et al.* reported on a record of 7.6% cell efficiency using a EMIB(CN)<sub>4</sub> based binary-ILs electrolyte in combination with the high molar extinction coefficient sensitizer K77 (Kuang *et al.*, 2004b). Hsui *et al.* prepared a binary IL electrolyte by dispersing TiO<sub>2</sub> nanoparticles for DSSCs and obtained a cell efficiency of 5.00% (Hsui *et al.*, 2004). Ikeda *et al.* investigated a clay-like conductive composite electrolyte (EOI/PACB) for DSSCs, which achieved a cell efficiency of 3.48% without the addition of iodine (Ikeda *et al.*, 2006). Zhao *et al.* (Zhao *et al.*, 2008) reported a solid-state DSSC utilizing imidazolium-type ionic crystal (MH-II) as transfer layer, and obtained a good cell efficiency of 3.1%. Besides, a new class of solid-state ionic conductor (SD) based on a carbazole-imidazolium cation structure was synthesized and investigated for application in all-solid-state DSSCs with a conversion efficiency of 2.85%.

We then focus on the IL electrolytes developed in our group for DSSCs and categorize them into three systems, namely, quasi-solid-state (system A), near-solid-state (system B), and all-solid-state (system C). In system A, among the discussed bi-ILs electrolytes, the DSSC containing BMISO<sub>3</sub>CF<sub>3</sub> achieved the best cell efficiency of 4.11%. The at-rest long-term stability of DSSCs with BMISO<sub>3</sub>CF<sub>3</sub> shows slight decay (lower than 5%) after being stored for more than 576 h. In system B, the near-solid-state DSSC with a non-volatile composite electrolyte, comprising PACB and the ionic liquid, PMII, without added iodine, showed a power conversion efficiency of 5.81%. A higher efficiency of 6.18% was achieved with the same composite electrolyte with the addition of EMISCN, the highest value for any iodine-free near-solid-state DSSC. At 70 °C the near-solid-state DSSC showed an unfailing stability (more than 1,000 h). In system C, efficient all-solid-state DSSC was developed using a hybrid SWCNT-binary CTI (EMII/PMII) without the addition of iodine and TBP, and achieved a high efficiency (3.49%). The DSSC with the hybrid SWCNT-binary CTI showed an excellent durability at room temperature for 1,000 h.

Nowadays, most quasi-solid state DSSCs with ionic liquid electrolyte achieved relatively low cell efficiency as compared to the traditional DSSCs with liquid electrolyte. Despite the former system possessed superior long-term stability than that of the latter, the cell efficiency indeed needs to be further improved. Thereby, the recent challenge in ILs based quasi-solid state DSSCs is on how to lower the viscosity of the ILs and to enhance the diffusion rate of the redox couples. This matter would be a key issue for future study.

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