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# **Solid-State Ionic Liquid Based Electrolytes for Dye-Sensitized Solar Cells**

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Additional information is available at the end of the chapter

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## **1. Introduction**

### **1.1. Dye-sensitized solar cells (DSSCs)**

The increasing global need for energy coupled with the depletion of easily accessible, hence cheap, fossil fuel reserves, poses a serious threat to the human global economy in the near future [1]. Considering in addition the harmful ecological impact of conventional energy sources, it becomes obvious that development of clean alternative energy sources is a necessity [2, 3]. Best renewable energy options must rely on a reliable input of energy onto the earth. Since the sun is our only external energy source, harnessing its energy, which is clean, non-hazardous and infinite, satisfies the main objectives of all alternative energy strategies. Mastering the conversion of sunlight to electricity or to a nonfossil fuel like hydrogen is without any doubt the most promising solution to the energy challenge. It is remarkable that a mere 10 min of solar irradiation onto the Earth's surface is equal to the total yearly human energy consumption [4]. Therefore, solar power is considered to be one of the best sustainable energies for future generations. To date photovoltaics has been dominated by solid-state junction devices, usually in silicon, crystalline or amorphous, and profiting from the experience and materials 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 solar cell based on interpenetrating network structures, such as dye-sensitized solar cells (DSSCs) [5].

Since Professor M. Grätzel in EPFL introduced the nanoporous films into dye-derived wide-band semiconductor research and made the breakthrough in the photoelectric conversion efficiency of DSSCs, academic and commercial interests have been focused on DSSCs for their high efficiency, potential low-cost and simple assembly technology. This became especially noticeable when the first cell with a certified efficiency of greater than 10% was demonstrated [6-10]. By incorporating the novel YD2-o-C8 dye and cosensitizing with Y123 dye, the DSSC with a traditional liquid electrolyte has achieved a 12.3% efficiency record [11], encouraging the surge to explore new organic materials for the conversion of solar to electric power.

The DSSC device is composed of three adjacent thin layers such as a high band-gap nanocrystalline semiconductor-based mesoporous film adsorbed with a dye sensitizer on the working electrode for the absorption in the visible region, a platinized counter electrode for the collection of electrons and a redox electrolyte, sandwiched between the two electrodes. The usual choice for the semiconductor material is titanium dioxide ( $\text{TiO}_2$ ), whereas ruthenium bipyridyl derivatives (N3, N719, Z907 and black dye etc.) are for the dye sensitizer. The electrolyte mostly contains  $\text{I}/\text{I}_3^-$  redox couple, which was obtained by the mixing of iodine ( $\text{I}_2$ ) and inorganic or organic iodides in suitable non-aqueous solvents. 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  $\text{TiO}_2$  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 ( $\text{SnO}_2:\text{F}$ ), on which the  $\text{TiO}_2$  film is formed. 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.

## 1.2. Ionic liquids (ILs)

Ionic liquids (ILs) are low-temperature molten salts with melting points below  $100\text{ }^\circ\text{C}$ , that is, liquids composed of ions only. The salts are characterized by weak interactions, owing to the combination of a large cation and a charge-delocalized anion. This results in a low tendency to crystallize due to flexibility (anion) and dissymmetry (cation). ILs are basically composed of organic ions that may undergo almost unlimited structural variations because of the easy preparation of a large variety of their components. Thus, various kinds of salts can be used to design the ionic liquid that has the desired properties for a given application. These include, among others, imidazolium, pyrrolidinium and quaternary ammonium salts as cations and bis(trifluoromethanesulphonyl)imide, bis(fluorosulphonyl) imide and hexafluorophosphate as anions.

An IL, triethylammonium nitrate (a pure low-melting salt), was firstly identified more than a century ago. In the 1930s, a patent application described cellulose dissolution using a molten pyridinium salt above  $130\text{ }^\circ\text{C}$ . It was the need for a sturdy medium for nuclear fuel re-

processing that prompted the study of low-melting-point chloroaluminates. Among the onium cations with positive nitrogen(s), those derived from the imidazolium ring proved to be the best choice in terms of melting points and electrochemical stability [12]. At the same time, the need for new anions for organic polymer electrolytes based on polyethylene oxide led to the concept of a plasticizing anion, that is, an anion having a delocalized charge and multiple conformations differing only marginally in energy. The archetype of such anions is the bis(trifluoromethylsulphonyl) amide ( $\text{CF}_3\text{SO}_2\text{-N-SO}_2\text{CF}_3$ ) ion, also known as  $\text{NTf}_2$ , in which the extremely electron-withdrawing  $\text{CF}_3\text{SO}_2$ -groups are conjugated and linked by flexible S-N-S bonds. When combined with an imidazolium cation, such as the ethylmethylimidazolium cation, this anion produces a fluid IL (melting point:  $-15\text{ }^\circ\text{C}$ ) with an ion conductivity comparable to that of the best organic electrolyte solutions; it shows no vapour pressure or no decomposition up to  $\sim 300\text{-}400\text{ }^\circ\text{C}$  [13]. It is not miscible with water ( $\sim 1,000$  p.p.m. in equilibrium with liquid  $\text{H}_2\text{O}$ ), and thus defies the conventional wisdom that states polarity is synonymous with hydrophilicity. ILs then developed rapidly, with a reinvestigation of ions, for example quaternary ammonium cations, that had been avoided previously by organic chemists because of unsymmetrical shapes that hindered easy purification through crystallization. The organic chemistry community had earlier engaged in research of media with controllable Lewis acidity (chloroaluminate ILs), but the modern era of ILs has produced numerous neutral ILs, that is, those based on ions which are unreactive towards acids or bases, be they Lewis or Bronsted. As a result, it is now difficult to name an organic reaction that has not been performed successfully in these potentially green solvents, which can be recycled almost indefinitely with no or minimal use of volatile organic compounds. Most products made in ILs can be distilled off, in the case of small molecules, or extracted with water or hydrocarbon solvents, at least one of which is usually immiscible with the ionic liquid.

It is this unique solvent potential that makes ILs key materials for the development of a range of emerging technologies. The advent of ILs has made viable processes that fail, or are even impossible, with conventional solvents. Water sensitive metals or semiconductors that previously could not be deposited from conventional water baths can now, by turning to ILs, be directly electroplated. Energy devices, such as the quasi-solid/all-solid-state DSSCs, polymer-electrolyte-membrane fuel cells, lithium batteries and supercapacitors presently under development to address the challenges of increasing energy costs and global warming, may greatly benefit from a switch to low-vapour-pressure, non-flammable, ILs-based electrolytes.

### 1.3. ILs as the electrolyte for DSSCs

The role of the electrolyte in DSSCs is very important as it provides the necessary ionic conductivity in the bulk of the solution and sets the potential barrier necessary for the energy conversion. In addition, it offers a reduction reaction at the counter electrode and helps for the dye regeneration by the charge-transfer reaction with the dye molecule [14]. Usually, the conventional inorganic and organic iodide electrolyte salts are lithium and tetra-alkyl ammonium iodides, respectively. Besides this, several molten salts, particularly ionic liquid

based imidazolium salts, have also been used for improving the performance of the DSSCs [15-19]. In these works, cations play an important role in determining the conversion efficiency of the DSSCs. For example, the interaction of  $\text{Li}^+$  with  $\text{TiO}_2$  enhances the electron transfer from the sensitized dye to the  $\text{TiO}_2$  and from  $\text{I}^-$  to the oxidized dye, leading to high photocurrent [20-22]. In the case of imidazolium cations, the increase in the concentration of imidazolium cations leads to the decrease of recombination at the working electrode due to the multilayer adsorption; thus improving the DSSC performance [23]. Kubo *et al.* [15] further studied the effect of the alkyl chain length of some imidazolium cations on the electron recombination lifetime. They found that the chain length does affect the electron recombination lifetime. The lifetime increased with the increase in the alkyl chain length. This is because hydrophobic alkyl chains may impede  $\text{I}_3^-$  from reaching  $\text{TiO}_2$ . The result reveals that bigger cations may enhance photocurrent due to the lower probability of electron recombination.

The highest efficiency record of DSSC was obtained based on the highly volatile organic solvent electrolyte due to the efficient infiltration of organic electrolyte in nanocrystalline films. However, commercialization of the cells with organic liquid electrolytes was impeded owing to technological problems related to hermetic sealing, precipitation of salts at low temperature and evaporation of liquids at high temperature; long-term stability is thus a major problem for these types of cells. Therefore, p-type inorganic semiconductors [24-26], organic hole conducting materials [27-30], ionic gel electrolytes having a polymer or a gelator [15, 31-33], and ionic liquid (IL) based electrolytes (or IL based electrolyte containing dispersed nano-components) [18, 34-40] were recently investigated for preparing the electrolytes. In these cases, imperfect filling of the dye-coated porous  $\text{TiO}_2$  film by p-type inorganic semiconductors or polymers has resulted in poor efficiency for the cells. Another weakness of the inorganic p-type materials is the decided chemical structure, resulting in the limitedly adjustable chemical/physical properties in the application of solid-state electrolytes. Meanwhile, the inorganic p-type material derived all-solid-state DSSCs shows no stability. This should be ascribed to inorganic p-type materials tending to be oxidized under continuous illumination and the worsening of the interfacial contact between dye-sensitized  $\text{TiO}_2$  and electrolyte along with the growth of age [41]. Moreover, the carrier diffusion length was limited in the case of conducting polymers due to their low conductivity. Thereby, ILs based electrolytes were considered to be most attractive for replacing the organic solvents; they are preferred because of their negligible vapor pressure, high thermal stability, wide electrochemical window, and high ionic conductivity [42-46]. However, most ILs based electrolytes are liquid at room temperature [36, 43, 45-48]. Therefore, the fluidity and potential leakage of ILs based electrolytes during long-term operation is still unavoidable, which limits their wide application in DSSCs. To overcome this problem, the solid-state ILs have been applied as solid-state electrolytes for DSSCs recently.

This chapter mainly reviewed the recent researches on the topic of solid-state ILs-based electrolytes for DSSCs. Here the solid-state ILs employed in the electrolytes of DSSCs can be classified as follows: (a) ILs crystals (system A), (b) ILs polymers (system B), and (c) ILs conductors (system C).

## 2. Solid-state ILs-based electrolytes for DSSCs

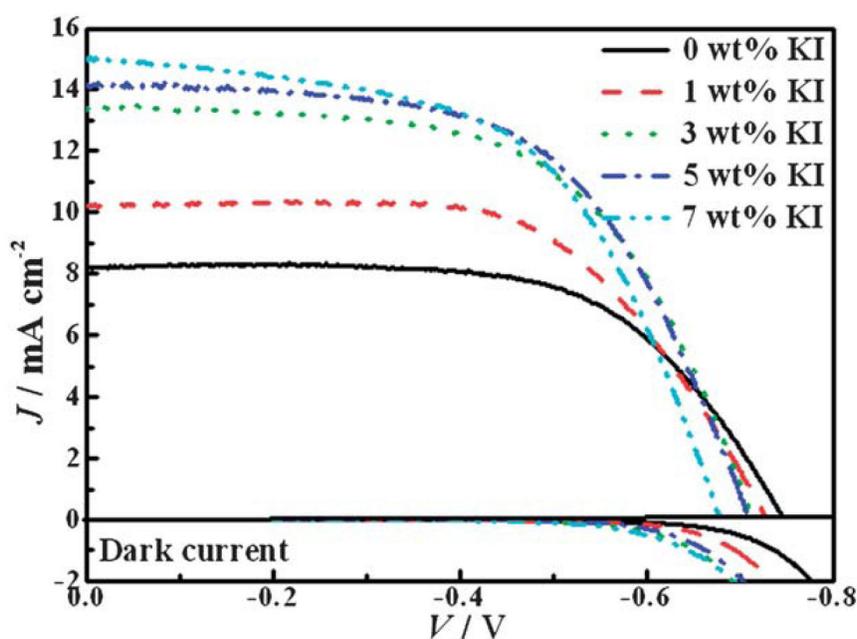
### 2.1. ILs crystals (system A)

In year 2005, Yamanaka *et al.* [49] reported a new strategy for enhancing the conductivity of ILs based electrolytes; employing an IL crystal as a constituent of an electrolyte, which forms a self-assembled structure and promotes the exchange reaction by the locally increased concentrations of  $I_2$  and  $I_3^-$  [15, 50]. They selected 1-dodecyl-3-methylimidazolium iodide (C12MImI) as the IL crystal. This provides a self-assembled structure of the imidazolium cations like a solid, while maintaining the molecular dynamics like a liquid. The IL crystal (C12MImI) with the smectic A phase (SA) has a bilayer structure of interdigitated alkyl chains of the imidazolium cations, and  $I_2$  and  $I_3^-$  would be localized between the SA layers. The locally high concentration would promote the exchange reaction. So, the IL crystal with the SA phase would be suitable for the electrolyte of DSSC. A few examples of the IL crystal with the SA phase, such as imidazolium salts consisting of cations with alkyl chains of C12-C18 and anions of hexafluorophosphate or bromide, have been reported [51, 52]. Before their study [49], an imidazolium salt with iodide as the counter anion has not been reported to be an IL crystal with a SA phase. Therefore, they showed for the first time that imidazolium iodides with alkyl chains longer than C12 exhibit a SA phase and that the liquid crystalline nature is preferable in terms of the hole transport layer in DSSC. The DSSC with C12MImI/ $I_2$  electrolyte achieved a cell efficiency ( $\eta$ ) of 2.30% under AM 1.5 irradiation. Zhao *et al.* [53] reported a solid-state DSSC utilizing imidazolium-type ionic crystal (1-methyl-3-hydroxyethyl-imidazolium iodide, MH-II) as the charge transfer layer, and obtained a good cell efficiency of 3.10% under one sun irradiation by adopting 1-methyl-3-propylimidazolium tetra-fluoroborate (MP-BF<sub>4</sub>) as a crystal growth inhibitor, lithium bis-trifluoromethanesulfonylimideas (Li[(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N]) a charge transport enhancer, and 4-tert-butylpyridine (tBP) as a carrier recombination inhibitor. As shown in their report, the cell efficiency remained 60% of the initial value after 30 days at room temperature (R. T.) without any sealing and protection from ambient condition. Lee *et al.* [54] have fabricated all-solid-state DSSCs with a hybrid SWCNT-binary charge transfer intermediate (CTI), consisting of single wall carbon nanotubes (SWCNT), 1-ethyl-3-methylimidazolium iodide (EMII) and 1-methyl-3-propyl imidazolium iodide (PMII), without the addition of  $I_2$  and tBP. A solid organic ionic crystal, EMII, was employed as CTI to fabricate all-solid-state DSSCs. In addition, SWCNTs were incorporated into the CTI as the extended electron transfer materials (EETM), which can reduce charge diffusion length and serve simultaneously as catalyst for the electrochemical reduction of  $I_3^-$ . An all-solid-state DSSC with this hybrid SWCNT-EMII achieved the higher cell efficiency (1.88%), as compared to that containing bare EMII (0.41%). To further improve the cell efficiency, they utilized PMII, which acts simultaneously as a co-charge transfer intermediate and crystal growth inhibitor. The highest cell efficiency (3.49%) was obtained using a hybrid SWCNT-binary CTI. In their studies, the durability of the solid-state DSSCs were studied at R. T. and was found to be far superior to that of a cell with an organic solvent electrolyte. In their further study, Lee *et al.* [55] also developed a solid-state composite electrolyte, comprising two ionic liquids and a carbon material, to fab-

ricate a solid-state DSSC; the ILs were EMII and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF<sub>4</sub>), and the carbon materials were carbon black (CB), multi-wall carbon nanotubes (MWCNT), and single-wall carbon nanotubes (SWCNT). A cell efficiency of 0.41% was achieved by using the bare EMII as the CTI; an efficiency of 2.52% was achieved for a solid-state DSSC by the incorporation of carbon black (CB) in the EMII. To further improve the cell efficiency, they utilized EMIBF<sub>4</sub>, a crystal growth inhibitor, as an additive to the electrolyte. A cell efficiency of 3.09% was obtained using an electrolyte containing the CB and the binary CTI (EMII plus EMIBF<sub>4</sub>). When the CB was replaced with MWCNT and SWCNT, the cell efficiency could be improved to 3.53% and 4.01%, respectively. Long-term durability of the DSSC with SWCNT-binary CTI was found to be far superior to that of the cell with an organic solvent electrolyte, and in fact the durability was uninterrupted for at least 1,000 h. Armel *et al.* [56] have developed the organic ionic plastic crystals as a new class of solid-state electrolyte for DSSCs. The DSSC with their solid-state electrolyte, containing N,N-dimethylpyrrolidinium dicyanamide (C<sub>1</sub>mpyrN(CN)<sub>2</sub>), EMII, lithium iodide (LiI), I<sub>2</sub> and N-methylbenzimidazole (NMB), achieved a good cell efficiency of 5.10% under the illumination of 1 sun (AM 1.5G). Among the system A, Chen *et al.* [57] have developed a most efficient solid-state electrolyte employing an ionic liquid (1, 2-dimethyl-3-propylimidazolium iodide, DMPII) as CTI for DSSCs. Simultaneously, potassium iodide (KI) and polyethylene oxide (PEO, MW = 100,000) were incorporated into the CTI as the charge transfer auxiliary agent and the crystal growth inhibitor, respectively. Where, the strong interactions between the potassium cations and PEO can prevent the crystallization of the CTI and then enhance its ionic conductivity. As shown in Figure 1, an optimal cell efficiency of 5.87% can be obtained for the DSSC fabricated with the solid-state electrolyte of DMPII/KI/PEO. The corresponding photovoltaic parameters of the DSSCs with their solid-state electrolyte containing different KI contents are listed in Table 1. Recently, Li *et al.* [58] also reported the development of organic ionic plastic crystals, instead of molecular plastic crystals (such as succinonitrile), as the electrolytes for solid-state DSSCs. Compared with molecular plastic crystals, the advantages of ionic plastic crystal materials are their higher conductivity and very low volatility [59]. In their work, 1-ethyl-1-methylpyrrolidinium bis(tri-fluoromethane sulfonyl)imide (P<sub>12</sub>TFSI), a well-known example of an organic ionic plastic crystal [40, 60-62], which shows a broad solid–solid transformation at 14 °C (entropy of transition 3.1 J K<sup>-1</sup> mol<sup>-1</sup>) and a melting point at 86 °C, was applied as the electrolyte for solid-state DSSCs. A room-temperature (R.T.) IL, PMII, was used as the iodide source for the electrolyte. The DSSCs with P<sub>12</sub>TFSI/PMII electrolyte yielded a cell efficiency of 3.92% under the illumination of 100 mW cm<sup>-2</sup> (AM 1.5G). Further addition of LiI and N-butylbenzimidazole (NBB) to the P<sub>12</sub>TFSI/PMII electrolyte improved the cell efficiency to 4.78%. Their DSSCs, using P<sub>12</sub>TFSI/PMII/LiI/NBB electrolyte, displayed better long-term stability compared to conventional liquid electrolytes, and remained 90% of the initial value after 50 days under ambient conditions without further sealing. Cao-Cen *et al.* [63] have synthesized the organic ionic crystal (N-4-(4-cyanobiphenyl-40-oxy)-butyl-3-butylimidazolium bromide, C<sub>4</sub>BImBr) carrying 4-cyano-4'-hydroxybiphenyl and imidazolium units and applied them as the electrolytes for DSSCs. It has been demonstrated that biphenyl and 4-cyanobiphenyl are important core units for mesogenic molecules [64-67]. Cyanobiphenyl-functionalized compounds can act as

a kind of low light-transmitting and high light-scattering material and obtained a high light-harvesting efficiency when they were employed as an electrolyte placed at the back of the working electrode of DSSC. The fabricated all-solid-state DSSCs with EMII/I<sub>2</sub>/C<sub>4</sub>BImBr electrolyte achieved a good cell efficiency of 4.45% under the illumination of 100 mW cm<sup>-2</sup> (AM 1.5G) because of the enhanced light harvesting capability of the electrolyte containing C<sub>4</sub>BImBr. To further improved the cell efficiency, PMII, was added into the EMII/I<sub>2</sub>/C<sub>4</sub>BImBr electrolyte as a crystal growth inhibitor. This fabricated DSSC with EMII/I<sub>2</sub>/C<sub>4</sub>BImBr/PMII electrolyte showed an enhanced cell efficiency of 5.07% under the illumination of 100 mW cm<sup>-2</sup> (AM 1.5G), and it also possessed a good long-term stability (decay 5%) for 1,000 h during the accelerated aging test (1sun light soaking) at 25 °C.

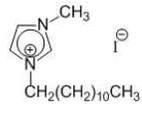
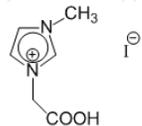
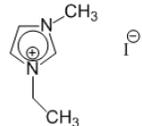
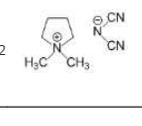
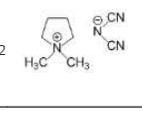
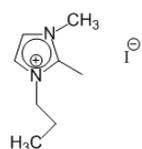
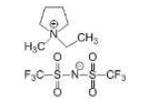
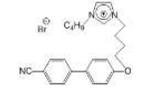
Table 2 is a partial list of the all-solid-state DSSCs with ILs crystals-based electrolytes, which were obtained from the literatures.



**Figure 1.** Photovoltaic characteristics of DSSCs assembled with the quasi solid-state electrolyte containing different KI contents under 100 mW cm<sup>-2</sup> and in the dark [57].

KI (wt%)	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (mV)	FF	$\eta$ (%)
0	8.22	750	0.65	4.05
1	10.21	730	0.61	4.56
3	13.44	710	0.59	5.66
5	14.11	710	0.59	5.87
7	15.00	680	0.56	5.72

**Table 1.** Photovoltaic characteristics of DSSCs assembled with the quasi solid-state electrolytes containing different KI contents under 100 mW cm<sup>-2</sup>.

References	ILs crystals	Structures	Electrolytes	Dye	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (mV)	FF	$\eta$ (%)	Durability
Yamanaka et al., (2005)	C12MImI		C12MImI; I <sub>2</sub>	N. A.	~7.00	~520	~0.63	~2.30	N. A.
Zhao et al., (2008)	MH-II		MH-II; MP-BF <sub>4</sub> ; Li[(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N] ; tBP	N3	7.01	646	0.69	3.10	30 days at-rest at 25 °C, decay 40%
Lee et al., (2010)	EMII		EMII; PMII; SWCNTs	N719	8.07	716	0.61	3.49	1,000 h at-rest at 25 °C, no decay
Lee et al., (2011)	EMII		EMII; EMIBF <sub>4</sub> ; SWCNTs	N719	9.74	620	0.66	4.01	1,000 h at-rest at 25 °C, no decay
Armel et al., (2011)	EMII		C <sub>1</sub> mpyrN(CN) <sub>2</sub> ; EMII; LiI; I <sub>2</sub> ; NMB	N719	8.60	775	0.77	5.10	N. A.
Chen et al., (2011)	DMPII		DMPII; KI; PEO	N719	14.11	710	0.59	5.87	N. A.
Li et al., (2012)	P <sub>12</sub> TFSI		P <sub>12</sub> TFSI; PMII; LiI; NBB	Z907	12.45	588	0.65	4.78	50 days at-rest at 25 °C, decay 10%
Cao-Cen et al., (2012)	C <sub>4</sub> BlmBr		EMII; I <sub>2</sub> ; C <sub>4</sub> BlmBr; PMII	Z907	12.39	609	0.67	5.07	1,000 h light soaking at 25 °C, decay 5%

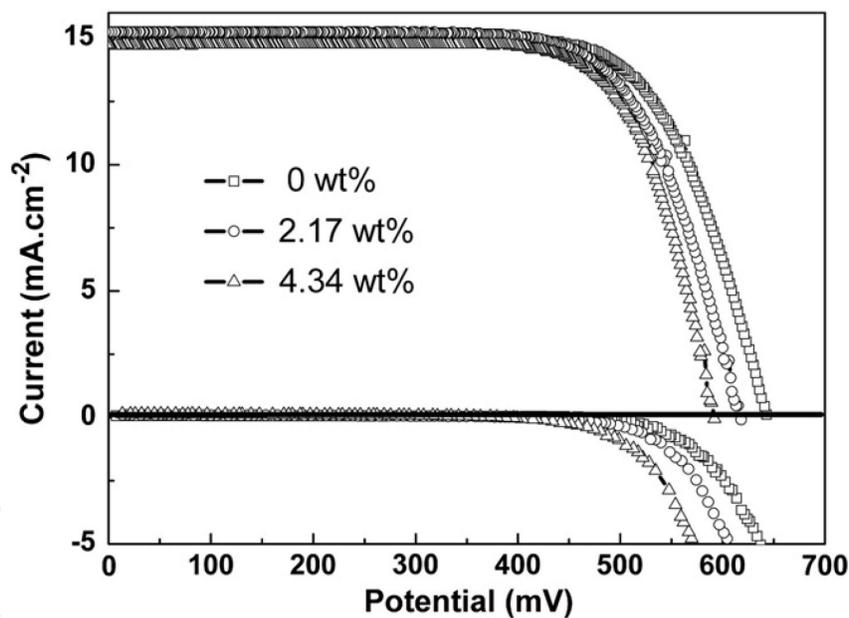
**Table 2.** Partial literatures reported on the solid-state DSSCs with ILs crystals.

## 2.2. ILs polymers (system B)

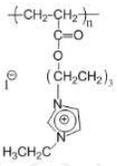
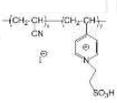
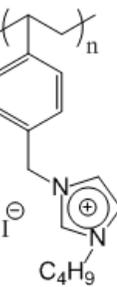
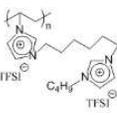
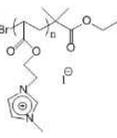
Wang *et al.* [68, 69] have synthesized the IL polymers, poly(1-alkyl-3-(acryloyloxy)hexylimidazolium iodide) (PAAII) and employed it as an iodine-free electrolyte for all-solid-state DSSCs. PAAII is an ionic liquid polymer formed from the polymerization of monomers containing IL moieties [70, 71]. IL polymers contain both the IL structure and the polymer main chain. They show good ionic conductivity without liquid components due to their specific functions such as transport of target ions, specific polar environment and mechanical strength [72]. They used poly(1-ethyl-3-(acryloyloxy)hexylimidazolium iodide) (PEAII) as the electrolyte without the addition of iodine, a cell efficiency of 5.29% has been achieved in solid-state DSSCs under illumination of 100 mW cm<sup>-2</sup> (AM 1.5G). PEAII also exhibited high thermal stability, and the DSSC assembled with PEAII electrolyte maintained about 85% of their initial efficiency after 1,000 h without sealing. An acidic ionic liquid polymer P [((3-(4-vinylpyridine) propanesulfonic acid) iodide)-co-(acrylonitrile)], which is named as P-HI for short, has been synthesized and employed in ILs electrolyte for DSSCs by Fang *et al.* [73]. The polymer P-HI contains sulfonic acid group, which has electrostatic forces with ILs to form the homogeneous and continuous framework for enhancing transportation of redox couples in the electrolyte. The DSSC with the novel ILs electrolyte, containing P-HI, NMB, guanidinium thiocyanate (GuNCS), 1-hexyl-3-methylimidazolium iodide (HMII) and 1-allyl-3-methylimidazolium iodide (AMII), achieved the highest cell efficiency of 6.95% under AM 1.5G illumination at 100 mW cm<sup>-2</sup> in the system B. They also investigated the effects of the concentration of iodine on the performance of DSSCs with their electrolyte system. As shown in Figure 2, they found that the addition of iodine mainly reduces the open-circuit voltage ( $V_{oc}$ ) and slightly decreases the short-circuit current density ( $J_{sc}$ ) of their cells due to the increase in dark current and the serious visible light by  $I_3^-$ , respectively. Therefore, they demonstrated that their system works best without the addition of iodine. Chi *et al.* [74] have synthesized a polymerized ionic liquid of poly((1-(4-ethenylphenyl)methyl)-3-butylimidazolium iodide) (PEBII) and employed it as a solid electrolyte for I<sub>2</sub>-free solid-state DSSCs. In their study, the photoanode/electrolyte interfaces were significantly improved using a graft copolymer-directed and organized mesoporous TiO<sub>2</sub> thin film. The cell efficiency of the DSSC with PEBII has reached 5.93% at 100 mW cm<sup>-2</sup>. In their further study [75], they utilized a novel TiO<sub>2</sub> photoanode with double layer structures containing mesoporous TiO<sub>2</sub> beads and PEBII electrolyte for constructing an solid-state DSSC; the cell efficiency was then enhanced up to 6.70%. Bis-imidazolium based poly(ionic liquid), poly(1-butyl-3-(1-vinylimidazolium-3-hexyl)-imidazolium bis(trifluoromethanesulfonyl)imide) (Poly[BVIm][HIm][TFSI]), was synthesized by Chen *et al.* [76], and it was dissolved in the ILs electrolyte (EMII/PMII/1-ethyl-3-methylimidazolium thiocyanate (EMISCN)/I<sub>2</sub>/GuSCN/N-butylbenzimidazole (NBB)) to form solid-state electrolytes for DSSCs, without using any volatile organic solvent. They found that the bis-imidazolium based Poly[BVIm][HIm][TFSI] electrolyte possessed good thermal stability and conductivity due to the charge transport networks formed in the electrolyte via the  $\pi$ - $\pi$  stacked imidazolium rings. The DSSCs based on Poly[BVIm][HIm][TFSI] electrolyte yielded the cell efficiency of 5.92% under the simulated AM 1.5G solar spectrum illumination at 100 mW cm<sup>-2</sup>. The Poly[BVIm][HIm][TFSI] based DSSC also showed a good long-term stability during accelerated aging test under 1 sun light-soaking at

60 °C, and it retains about 96% of the initial efficiency even after about 1,200 h test. In the recent report from Chang *et al.* [77], multi-walled carbon nanotubes (MWCNT) coated with a thin layer of 1-(2-acryloyloxy-ethyl)-3-methyl-benzoimidazol-1-ium iodide (AMBIImI) were successfully fabricated by physical adsorption. They were then incorporated into poly(1-(2-acryloyloxy-ethyl)-3-methyl-imidazol-1-ium iodide (poly(AMImI))-based electrolytes to fabricate an all-solid state DSSC. The DSSC with the solid-state electrolyte, containing, achieved a cell efficiency of 3.55% at  $100 \text{ mW cm}^{-2}$ .

Table 3 is a partial list of the all-solid-state DSSCs with ILs polymers-based electrolytes, which were obtained from the literatures.



**Figure 2.** Photovoltaic characteristics of DSSCs using PH-I based electrolyte containing different contents of iodine measured under  $100 \text{ mW cm}^{-2}$  and in the dark [73].

References	ILs crystals	Structures	Electrolytes	Dye	$J_{sc}$ (mA cm <sup>-2</sup> )	$V_{oc}$ (mV)	FF	$\eta$ (%)	Durability
Wang <i>et al.</i> (2011&2012)	PEAll		PEAll	N3	9.75	838	0.65	5.29	1,000 h at-rest at 25 °C, decay 15%
Fang <i>et al.</i> , (2011)	P-HI		P-HI; HMII; AMII; NMB; GuNCS	N3	15.10	643	0.72	6.95	N. A.
Roh <i>et al.</i> , (2012)	PEBII		PEBII	N719	16.60	760	0.53	6.70	N. A.
Chen <i>et al.</i> , (2012)	Poly[BVIm] [HIm][TFSI]		Poly[BVIm] [HIm][TFSI]; EMII; PMII; EMISCN); I <sub>2</sub> ; GuSCN; NBB	N719	12.92	676	0.68	5.92	1,200 h light soaking at 60 °C, decay 4%
Chang <i>et al.</i> , (2012)	Poly(AMImI)		Poly(AMImI); NMB; GuSCN; I <sub>2</sub> ; MWCNT- poly(AMImI)	N3	8.51	646	0.64	3.55	N. A.

**Table 3.** Partial literatures reported on the solid-state DSSCs with ILs polymers.

### 2.3. ILs conductors (system C)

Recently, Midya *et al.* [78] have designed and synthesized a new class of solid-state ionic conductors (Table 4) based on a carbazole-imidazolium ionic salt as electrolytes for solid-state DSSCs. Carbazole is chosen as the hole conductor because polyvinyl carbazole has already been employed successfully in a solid-state DSSC as a hole conductor [79]. In their report [78], the solid-state IL conductors with SCN<sup>-</sup> anions (SD1) or I<sup>-</sup> anions (SD2) were synthesized and applied in an all-solid-state DSSC. The solid-state electrolyte containing SD2 and I<sub>2</sub> can provide dual channels for hole/triiodide transportation (Figure 3). In their system (system C), the DSSC with a solid-state electrolyte, containing SD2, I<sub>2</sub>, Li[(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N], tBP and 1-ethyl-3-methyl-imidazolium tetracyanoborate (EMIB(CN)<sub>4</sub>), ach-



on a carbazole-imidazolium ionic salt as electrolytes for solid-state DSSCs. The DSSC with a solid-state electrolyte, containing SD2, I<sub>2</sub>, Li[(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N], tBP and EMIB(CN)<sub>4</sub>, achieved a cell efficiency of 2.85%. A literature survey on the solid-state DSSCs with IL-crystals, IL-polymers, and IL-conductors based electrolytes have shown that these systems possessed superior long-term durability over the traditional organic solvent based electrolytes.

Recently, the stable organic radical, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), was demonstrated to be a promising redox system for DSSCs [80, 81], offering an alternative to the widely used iodide/triiodide couple. In the future, we can synthesize a novel IL with TEMPO-imidazole complex [82-84] for an iodine (I<sub>2</sub>)-free mediator system, and make application on solid-state DSSCs. This kind of TEMPO-imidazole complex containing TEMPO-redox radical and iodide-redox anion could potentially provide dual channels for charge transportation within the DSSCs.

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