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# Ionic Liquid Enhancement of Polymer Electrolyte Conductivity and their Effects on the Performance of Electrochemical Devices

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Additional information is available at the end of the chapter

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## Abstract

Ionic liquids (ILs) are molten salts at ambient temperature and consist of poorly coordinating cations and anions. They have good electrical conductivity with a wide voltage window and high thermal stability, but negligible vapor pressure. ILs can enhance ionic conductivity when added to polymer electrolytes. Conductivity enhancement is due to the additional ions supplied by the IL, the plasticizing nature of the IL and the low viscosity that facilitates ion mobility. The plasticizing nature of ILs softens the polymer chain giving rise to easier polymer segmental motion. Increase in polymer segmental motion implies that IL can increase amorphousness of a polymer electrolyte (PE). This article discusses the involvement of ionic liquid as electrolytes in selected devices, namely dye sensitized photovoltaics, batteries, fuel cells and supercapacitors.

**Keywords:** polymer electrolyte, ionic liquid, dye-sensitized photovoltaic, supercapacitors, fuel cells

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## 1. Introduction

An ionic liquid (IL) is a molten salt at room temperature (RT). They consist of cations and anions that are weakly coordinating [1]. Ionic liquids (ILs) have thermal stability as high as 473–573 K, wide potential windows and high electrical conductivity [2].

ILs have low melting temperature and negligible vapor pressure. They are therefore green solvents making them suitable for applications in industries [3]. The negligible vapor pressure prevents loss of solvent to the environment. To economize space, abbreviations are used in this article. These are listed at the end of the article.

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## 2. ILs in polymer electrolytes (PEs)

ILs have been introduced in PEs for conductivity enhancement. Kumar and Hashmi [4] have introduced EMImTf, in PVdF-HFP- $\text{NaCF}_3\text{SO}_3$  PE system. EMImTf is a room temperature ionic liquid (RTIL). The PVdF-HFP with EMImTf PE system gave an electrical conductivity of the order  $10^{-1} \text{ S m}^{-1}$  at room temperature (RT), good thermal stability and wide potential window.

EMImBF<sub>4</sub> [5] has also been shown to increase ionic conductivity of PVdF-HFP-LiBF<sub>4</sub> PE system from  $4.4 \times 10^{-5}$  to  $2.0 \times 10^{-3} \text{ S m}^{-1}$ . The incorporation of EMImBF<sub>4</sub> introduced additional mobile ions namely EMIm<sup>+</sup> and BF<sub>4</sub><sup>-</sup>. This increased the concentration of mobile ions that is one of the parameters that govern ionic conductivity. The additional charge carriers also interacted with the electron donors of the polymer, which reduced the polymer-polymer intermolecular interaction. This will soften the polymer chains resulting in increased polymer segmental motion. Increased polymer segmental motion implied increased structural disorder or amorphousness of the PE system. Ion conduction only takes place in the amorphous region of the PE, hence with increased amorphousness, conductivity of the PE also increased.

The PP<sub>24</sub>TFSI ionic liquid has been added with LiTFSI to impart Li<sup>+</sup> ion transport [6]. The electrolyte displayed ionic conductivity of the order  $10^{-2} \text{ S m}^{-1}$  and potential stability window is 2.7 V versus Li<sup>+</sup>/Li. GPEs have also been successfully prepared by incorporating the Li<sup>+</sup>-IL mixture into PVdF-HFP. The GPE containing 80 wt. % IL solution attained an ionic conductivity of the order  $1 \text{ S m}^{-1}$  at 383 K.

The BMImBF<sub>4</sub> ionic liquid [7] conductivity was expected to decrease on addition of PVdF-HFP to the IL. This is because, on adding polymer to the IL will increase the IL viscosity. This should decrease the ionic mobility, and hence conductivity. However, the sample with 10 wt. % polymer and 90 wt. % IL exhibited RT conductivity which is higher than the pristine BMImBF<sub>4</sub>. This observation can be clarified successfully using the polymer breathing model. The model assumes that the polymer chains can open and fold. Chain opening is analogous to “inhaling” and chain folding to “exhaling”. This inhaling-exhaling process of the polymeric chain led to volume and local pressure changes that either dissociate ion pairs and increased number density of mobile ions or reduce viscosity and increased ionic mobility, both of which, will result in conductivity enhancement [8]. However, at high polymer content, viscosity effect would dominate.

One of the possible ways to determine the choice of an IL is by considering the type of alkyl chain. Different alkyl chains have different chain lengths. As an example, consider the three SPE samples chitosan/[C<sub>2</sub>mim][C<sub>n</sub>SO<sub>3</sub>], chitosan/[C<sub>2</sub>mim][C<sub>n</sub>SO<sub>4</sub>] and chitosan/[C<sub>2</sub>mim][diC<sub>n</sub>PO<sub>4</sub>]). [C<sub>2</sub>mim]<sup>+</sup> is the 1-ethyl-3-methylimidazolium cation [9] with sulfonate, sulfate and dialkylphosphate anions. The alkyl chains are determined by n. For the sulfonate anion, the subscript n values were 1, 2 and 4; for the sulfate anion, n values were 1 and 2 and n also had values of 1 and 2 for the dialkylphosphate anions. The highest conducting chitosan/[C<sub>2</sub>mim][C<sub>1</sub>SO<sub>3</sub>] sample exhibited a conductivity of  $7.78 \text{ S m}^{-1}$  at 298 K and  $0.75 \text{ S m}^{-1}$  at 373 K. Shorter alkyl chain length ILs exhibited higher conductivity due to their lower viscosity that facilitates ion mobility, hence higher conductivity. This can therefore be a method of choosing the appropriate IL for conductivity enhancement.

Another example of an IL-PE system consisted of PVA,  $\text{CH}_3\text{COONH}_4$  and BmImBr ionic liquid [10]. The IL increased the amorphousness of the polymer electrolyte and this enhanced ionic mobility. The plasticizing nature of the IL contributed to the softening of the polymer backbone that increased segmental motion. The segmental motion will bring a cation coordinated to the electron donor atom of the PVA near to another possible site and on compression of the chain, the cation can jump to the vacant site with low, but sufficient activation energy and will then be transported away from its former site as the segmental motion moves forward.

BMImTf was incorporated into a PEMA/PVdF-HFP blend with LiTf being the  $\text{Li}^+$  source [1]. The 49 wt. % PEMA-21 wt. % (PVdF-HFP)-30 wt. % LiTf exhibited an increase in RT maximum conductivity on addition of 60 wt. % BMImTf from  $2.9 \times 10^{-5}$  to  $8.59 \times 10^{-3} \text{ S m}^{-1}$ . At low BMImTf content, the number density of mobile ions was observed to influence the ionic conductivity, but the mobility and diffusion coefficient were more dominant at higher BMImTf contents. Incorporation of BMImTf also increased thermal stability. This is advantageous as the high decomposition temperature enables the polymer electrolyte to be used at elevated temperatures. The addition of BMImPF<sub>6</sub> into corn starch-based electrolyte with LiPF<sub>6</sub> salt also increased ionic conductivity [11]. This was attributed to the amorphousness of the sample.

We have shown that IL can enhance ion transport in an electrolyte. IL acts as a plasticizer, increased the amorphousness of a PE and the segmental motion of the polymeric chain. IL can also improve thermal stability.

### 3. ILs in dye-sensitized photovoltaic systems

Dye-sensitized solar cell (DSSC) is one of the third generation photovoltaic technologies that have been developed. It uses cheap materials that do not require tedious purifications, easy to fabricate and has high efficiency [12]. A DSSC consists of three main parts, namely (i) photoactive electrode or photoanode, (ii) Pt counter electrode and (iii) electrolyte with a redox mediator, for example,  $\text{I}^-/\text{I}_3^-$  as shown in **Figure 1**.

The DSSC mimics the process of photosynthesis. The sensitizer absorbs solar energy that excites the dye molecules and oxidizes them. The electrons released are injected into the mesoporous nano-TiO<sub>2</sub> conduction band (TiO<sub>2</sub> is normally used as part of the photoanode). After leaving the photoanode, the electrons move to the cathode where they reduce the  $\text{I}_3^-$  ions of the redox couple into  $\text{I}^-$  ions. The  $\text{I}^-$  ions then return the electrons to the oxidized dye molecules. The dye molecules are regenerated, the circuit is completed and current flows. The electrolyte is a key DSSC component. The high device photon to current efficiency is also associated with electrolyte conductivity. For a DSSC with  $\text{I}^-/\text{I}_3^-$  redox couple, the contribution to conductivity by the  $\text{I}^-$  ions is important. IL can be used to increase the iodide mobility, which may result in high DSSC efficiency.

An EMImI ionic liquid has been employed in a DSSC. However, EMImI can easily crystallize and this will prevent them from entering the pores of the nanocrystalline semiconducting TiO<sub>2</sub> films. In order to inhibit EMImI from crystallizing, another type of IL, TIPIL can be added to EMImI electrolyte [13]. Hence, without TIPIL and if EMImI crystallizes, the photon to electricity conversion efficiency will be low [14]. The electrolyte containing TIPIL had

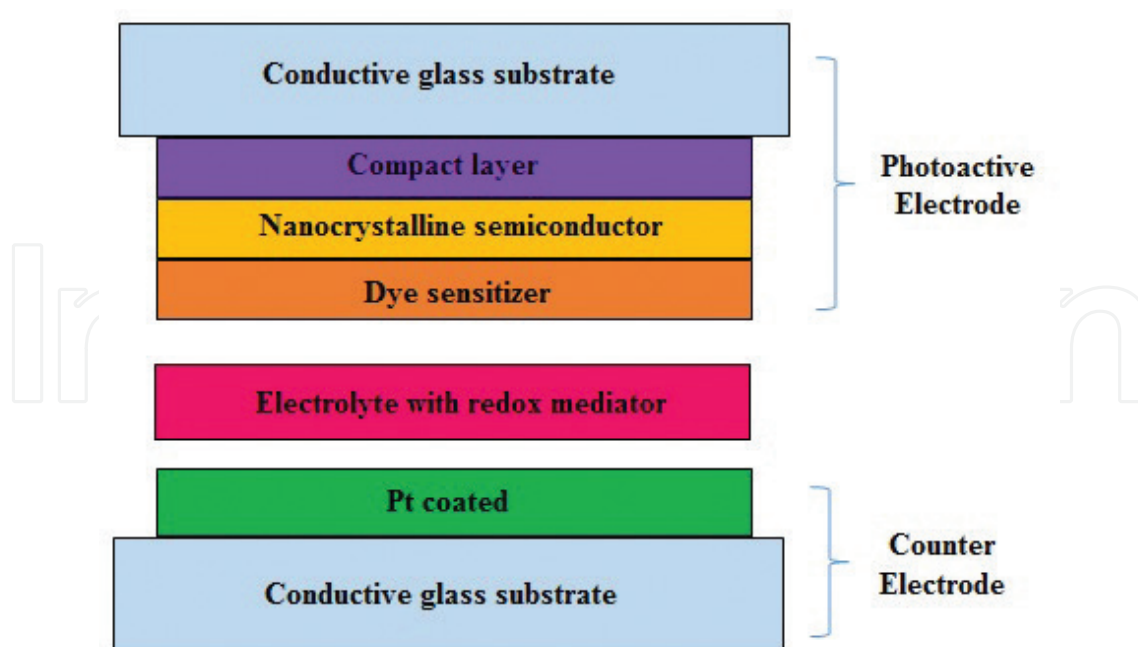


Figure 1. Configuration of DSSC.

improved the photovoltaic efficiency of the DSSC to 5.37%, which was about an 18% increase in efficiency compared to the DSSC without TIPIL. The inhibiting effect toward EMImI crystal growth decreased surface tension between EMImI and the dyed-TiO<sub>2</sub> films and improved interfacial wetting. The stability of the cell was also improved and thus able to maintain more than 90% of the initial efficiency after the aging test. The device using EMImI with I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox mediator electrolyte without TIPIL exhibited a decrease of durability in less than 10 days. Hence the use of a crystallizing inhibiting IL can help to maintain stability of the DSSC.

Imidazolium iodide ILs have been used widely as a solvent in electrolytes containing I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox mediator for the fabrication of DSSCs [11–15]. However, the high viscosity of pure imidazolium iodide IL can obstruct diffusion of the I<sup>-</sup> and I<sub>3</sub><sup>-</sup> ions of the mediator, thus limiting solar cell performance [15]. Also, if the I<sup>-</sup> concentration is large, the dye molecules that have been excited (D\*) can be reduced by the iodide ions, forming reduced dye molecules (D<sup>-</sup>) and iodine radicals I• following the reaction [16]



The reduced dye molecules can either inject the electrons into the TiO<sub>2</sub> following the equation



and this leads to photocurrent which will be benefit the device performance. The reduced dye can also react with an I<sub>3</sub><sup>-</sup> ion according to the equation below.





This is a recombination reaction that will result in electron loss and is “parasitic” to the DSSC performance because it can result in a decrease in photocurrent. If this happens, it implies that recombination reaction is dominant over electron injection and cell efficiency will be reduced. Hence, to reduce I-ion concentration and viscosity of the electrolyte, binary or double ILs were used in electrolyte preparation [17–20] and this can avoid efficiency loss.

Since iodine has a negative effect on the efficiency when used in large concentrations, liquid electrolytes free from iodine had to be prepared [17]. Iodine in the electrolyte gives rise to polyiodides such as  $I_3^-$  or  $I_5^-$  according to the equation:



At high iodine content, polyiodide concentration in the mesoporous dyed-TiO<sub>2</sub> matrix will also increase. Polyiodides can assist electron recombination and also aid in solar cell increasing dark current. A high I<sub>2</sub> content can also result in enhanced light absorption by the carrier mediator. This will make the dye molecules harvest less light and led to the decrease in  $V_{oc}$  and  $J_{sc}$ .

DSSCs with configuration FTO (fluorine tin oxide)/photoanode/IL-CB/Pt/FTO and FTO/photoanode/IL-PACB/Pt/FTO have been fabricated [21]. The electrolytes were I<sub>2</sub>-free. Here CB stands for carbon black and PACB for polyaniline-loaded carbon black. FTO or fluoride tin oxide was the current collector. The IL was either BMImI or MPImI. With CB, the efficiencies exhibited were 4.38% (MPImI/CB) and 3.68% (BMImI/CB). The MPImI/PACB containing cell exhibited an efficiency of 5.81% under 1 Sun illumination. The working of the I<sub>2</sub>-free DSSC is similar to the I<sub>2</sub> containing DSSC, but the  $I_3^-$  ion was formed by iodide oxidation. The IL in the electrolyte can provide sufficient I<sup>-</sup> anion that under illumination



Hence, I<sup>-</sup> anion can be oxidized to  $I_3^-$  anion and the redox couple is generated.

DSSC using PACB has been investigated at RT and at 343 K. Its performance was superior to a DSSC using organic solvent electrolyte.

Another type of gel electrolyte that is I<sub>2</sub>-free has been prepared using a mixture of KI and DMPIImI that has been gelled [22]. The DSSC employing the GPE achieved a photon conversion efficiency of 6.44%. The I<sub>2</sub>-free gel electrolyte was able to reduce electron recombination and solar cell dark current. The I<sub>2</sub>-free electrolyte system demonstrated a method to be used in the fabrication of DSSCs for performance improvement.

As IL is considered a “green” solvent, it has also been applied in the DSSCs with natural dyes as sensitizer [23]. The electrolyte was 2.33 wt. % functionalized alkoxide precursor + 47.24 wt. % sulfolane + 23.62 wt. % 3-methoxypropionitrile + 10.87 wt. % AcOH + 3.54 wt. % LiI + 3.54 wt. % MPImI + 1.77 wt. % I<sub>2</sub> + 6.02 wt. % TBP + 1.06 wt. % GuSCN. TBP and GuSCN were introduced to help increase  $J_{sc}$  as well as  $V_{oc}$ .

IL is often used in devices as electrolyte, but fabrication of devices using liquid electrolytes (LEs) is difficult. LEs are volatile and may leak [24, 25]. This will cause the electrode to corrode

and the dye to decompose in the medium [26, 27]. On top of these, sealing and stability problems are also associated with LEs [28, 29]. The use of IL, though beneficial is not leakage-proof due to its liquid state. To overcome this, IL can be added into polymers [30–35], gelators [24, 36] and nanoparticles [37] to form gel or quasi-solid-state electrolytes. The use of gel electrolytes solves electrolyte leakage problem, enhances robustness and increases stability [38]. According to Ref. [39], a gel-type membrane is obtained when an IL solution is immobilized in a polymer matrix. The solvents trapped in the host polymer exhibit good electrolyte conductivity. Electrolyte-photoanode and electrolyte-cathode contacts were also improved. This will also contribute to improve efficiency of the DSSCs [25, 40]. Gel electrolyte is also an alternative to replace solid electrolytes in DSSC. This is because solid electrolyte cannot fill the pores of the nanosemiconducting mesoporous  $\text{TiO}_2$ . This causes dye regeneration problems, recombination enhancement and efficiency lowering [2].

The  $\text{PEO:KI:I}_2$  membrane has been added with EMImTFSI. The IL has low viscosity of 0.034 Pa S at 298 K. The IL increased ionic conductivity of the membrane and improved efficiency of DSSC [41]. The conductivity increase can be accredited to the charge carriers supplied by the IL. The IL also increased amorphousness of the electrolyte. Adding another IL of low viscosity, namely, (EMImTf) into a  $\text{PEO:NaI:I}_2$  system [42] reduced crystallinity and enhanced the ionic conductivity. As for the DSSC performance, the addition of EMImTf enhanced  $J_{\text{sc}}$  by about four times and the solar cell efficiency by more than three times. This work seems to show that mobility of the iodide ions and efficiency are related. By adding EMImDCN into a PEG plasticized  $\text{PEO:NaI:I}_2$  system, the performance of DSSC improved from 0.74% with no IL to 3.02% at 1 Sun illumination. This again showed conductivity-efficiency relationship and the role of IL as plasticizer [43].

PAN-based GPEs have been prepared using three salts, namely, LiI,  $\text{Pr}_4\text{NI}$  and BMImI IL. The highest RT conductivity was  $0.393 \text{ S m}^{-1}$  [28]. When used in DSSC with mesoporous  $\text{TiO}_2$ , the cell exhibited  $J_{\text{sc}}$  of  $206 \text{ A m}^{-2}$  and efficiency 5.41%. The efficiency,  $V_{\text{oc}}$  and  $J_{\text{sc}}$  varied with electrolyte composition. These can be explained based on  $\text{Li}^+$  and  $\text{Pr}_4\text{N}^+$  adsorption on the mesoporous  $\text{TiO}_2$  surface that shifted the Fermi level of the semiconductor to a more positive or negative energy level that would certainly affect electron injection into the  $\text{TiO}_2$  conduction band and  $J_{\text{sc}}$  and the  $V_{\text{oc}}$ , since the distance between the Fermi and the redox mediator levels can be shortened or lengthened. The ternary iodide electrolyte that includes LiI,  $\text{Pr}_4\text{NI}$  and BMImI ionic liquid uncovers the advantage of a ternary system that has been shown to increase the DSSC efficiency by 30%.

The DSSC [44] with GPE composed of P(VP-co-VAc), ethylene and propylene carbonates, KI and  $\text{I}_2$  also showed efficiency enhancement when MPImI ionic liquid was added. Again IL played the role as a plasticizing agent that increased the amorphousness of the electrolyte and eventuated in conductivity enhancement. The IL softened the polymer backbone, increased segmental mobility and provided new pathways for ionic motion. The large MPIm<sup>+</sup> cation enabled easier  $\text{I}^-$  anion dissociation that helped to increase  $J_{\text{sc}}$  as the MPImI concentration increased. The smaller  $\text{K}^+$  cation used in the same electrolyte reduced electron movement through the mesoporous nano- $\text{TiO}_2$  layer in the photoanode causing a shift in the  $\text{TiO}_2$  conduction band toward the redox potential. This led to increased  $J_{\text{sc}}$  and efficiency of the DSSCs.

Huo et. al [36] investigated quasi-solid-state DSSC (QS-DSSCs) prepared using the low molecular mass  $C_{18}H_{36}O_3$ .  $C_{18}H_{36}O_3$  is commonly used as gelling agent for organic solvents. The ILs studied were MPImI, MBImI and MHImI and were gelled with  $C_{18}H_{36}O_3$ . The electrolytes contained  $I_2$ , LiI and N-MBI in MPImI, MBImI and MHImI ionic liquids, respectively, to form ILGEs. The ILGEs with different  $Im^+$  cation alkyl chain lengths influenced adsorption competition between  $Im^+$  and  $Li^+$ , electron recombination or transport, charge diffusion,  $TiO_2$  conduction band shift and distribution of surface states. The ILGE containing  $Im^+$  cation with extended alkyl chain length can delay electron recombination, enhanced  $J_{sc}$  and improves IPCE. The DSSC with MHImI exhibited the highest efficiency of 3.25%. All DSSCs based on ILGEs exhibited stable photovoltaic performance.

Electrolyte solidification may solve problems associated with leakage of organic solvents. However, issues associated with evaporation and toxicity still limit the DSSCs long-term operation. To overcome problems due to toxicity and evaporation, the use of low viscosity ILs were suggested. ILs can also dissolve polysaccharides and biomacromolecules. It has been shown [38] that a DSSC using a solvent free  $LiI + I_2 + BMImI + EMiDCA + TBP$ -based solidified electrolyte exhibited efficiency of ~4%. Electrolyte solidification can also be done using synthetic polymers.

GPEs are electrolytes that contain mobile cations and anions. Thus the electrolyte can be polarized. For example, since in DSSCs with iodide/triiodide redox mediators require iodide ion conductivity, it would be useful to “immobilize” the cations and increase the anion transport or transference number [35]. This has led to the synthesis of an electrolyte in which, the cation is constrained to the polymer backbone. This is known as a PIL. A PIL with the cation constrained to the polymer backbone is therefore a single ion conductor. A DSSC using PMAPII as the PIL-based GPE and PEDOT-NF as the counter electrode has been reported in Ref. [45]. The transference number of the imidazolium cations is reduced due to their being immobilized, but the iodide anions can easily migrate. The PIL formed a stable GPE with increased  $I^-$  transference number. The most conducting electrolyte ( $0.49\text{ S m}^{-1}$ ) contained 16 wt. % PMAPII. The DSSC with the PIL GPE and PEDOT-NF electrode showed 8.12% efficiency. The performance was better than the liquid electrolyte DSSC and Pt counter electrode that exhibited an efficiency of 7.20%.

An IL-imbibed polymer gel electrolyte has been designed [46] using an IL solvent, an IL iodide source and a polymer. The solvent was BMImCl. The iodide source was MPImI ionic liquid and poly(HEMA/GR), a hydrophilic and lipophilic host matrix. The host matrix possesses unique microporosity, extraordinary absorption and good electrolyte loading and retention to form a stable gel. The interconnected poly(HEMA/GR) framework stores the IL electrolyte. The GPE had high room temperature conductivity and good stability. The DSSC exhibited 7.15% efficiency. This was higher than the 6% efficiency exhibited by DSSC employing acetonitrile-based electrolyte-imbibed in the same polymer host. The  $V_{oc}$  of the DSSC with the IL-imbibed GPE was 0.76 V and  $J_{sc}$  was 0.014 A. The product of  $V_{oc}$  and  $J_{sc}$  is  $106.2\text{ W m}^{-2}$ . The MPD was  $71.1\text{ W m}^{-2}$ . The electrolyte concept of imbibing IL into a polymer host indicates the potential application in DSSCs.

As another example, the solvent BMImNO<sub>3</sub> and the iodide ion supplier, MPImI, have been imbibed into poly(AA/GR) and poly(AA/CTAB) to form stable ion conducting medium in gel



form [47]. These polymer are also “hydrophilic and lipophilic” or amphiphilic. The imbibed poly(AA/GR) GPE exhibited RT electrical conductivity of  $1.78 \text{ S m}^{-1}$  and that of IL imbibed poly(AA/CTAB) GPE was  $1.84 \text{ S m}^{-1}$ . The efficiencies were 7.19% and 7.15%, respectively. The DSSCs employing acetonitrile-based GPEs with the same matrices exhibited lower efficiencies of less than 7%.

Besides imidazolium, other ILs based on sulfonium and ammonium have also been used in DSSCs. Sulfonium ion-based ILs mostly had higher conductivity than ammonium ion-based ILs due to their lower viscosity. DSSCs employing IL with asymmetric diethylalkylsulfonium cation,  $[\text{Et}_2(\text{n-C}_4\text{H}_9)\text{S}]^+$ , showed efficiency of 4.61% while DSSC using IL based on quaternary ammonium-based cations,  $[\text{Et}_3(\text{n-C}_8\text{H}_{17})\text{N}]^+$ , showed 3.95% efficiency [15]. This is due to the high charge-transfer conductivity.

The above examples illustrate how ILs have been used to improve conductivity and enhance DSSC performance.

#### 4. ILs in fuel cells

Fossil fuels cannot be renewed, pollute the environment and are the primary cause of global warming. To minimize some of these problems, it is necessary to produce energy using approaches that do not “destroy” the environment. One approach is to use hydrogen fuel cells in which water is a product besides electricity. Fuel cells are chemical to electrical energy converters. They are classed according to their operating temperature and electrolyte.

PEMFCs use hydrogen or methanol as the fuels. PEMFCs are used in transportation and also portable applications. PEMFCs have shown high electrical efficiency. They do not produce pollutant and they are easy to install. For application in PEMFC, the membranes should have high proton conductivity, good mechanical strength, dimensionally stable and good chemical, electrochemical and thermal stabilities [48].

Polymer electrolytes with addition of IL have been employed in fuel cells. Imidazolium type aprotic IL has been introduced into sulfonated poly (ether ketone) or SPEK for short. The electrolyte was prepared by solution casting [49]. The electrical conductivity was two orders of magnitude higher than the IL-free SPEK membrane even under anhydrous condition. The membrane was able to operate successfully under anhydrous condition between 313 and 413 K. The plasticizing effect of the ILs has made the electrolyte membrane flexible. The ability of the membrane to operate at 413 K shows its potential as a candidate for PEMFC. The same group has also prepared anhydrous  $\text{H}^+$  conducting composite membranes with BMImTf ionic liquid [50]. Under anhydrous condition, the  $\text{H}^+$  conductivity of the membranes was of the order  $10^{-1} \text{ S m}^{-1}$  between 303 and 413 K. The  $\text{H}^+$  conductivity increased with temperature and IL content. The  $T_g$  was observed to decrease implying that the IL has penetrated the polymer chains and enhanced segmental motion of the SPEK/ethylene glycol polymer.

The effects of IL cation on the PEMFC performance have been investigated by Gao et. al [51] using  $[\text{N1114}]^+$ ,  $[\text{Epdy}]^+$  and  $[\text{EMIm}]^+$  cations. The fuel cell worked poorly when the

imidazolium IL of [EmIm]HSO<sub>4</sub> was used as an electrolyte. The maximum current density was only 100 A m<sup>-2</sup>. The MPD was 16 W m<sup>-2</sup>. When the IL was replaced with non-imidazolium IL, [Epdy]HSO<sub>4</sub>, the current density increased to 700 A m<sup>-2</sup>. When [N1114]HSO<sub>4</sub> IL was employed, the current density drastically increased to around 1750 A m<sup>-2</sup> and the MPD increased to 650 W m<sup>-2</sup>. Fuel cell with [N1114]HSO<sub>4</sub> can work at 400 A m<sup>-2</sup> with voltage higher than 0.65 V for nearly 1 h without significant decrease in performance. To verify the better performance of [N1114]<sup>+</sup> and [Epdy]<sup>+</sup> ILs over [EMIm]<sup>+</sup>, calculations using Gaussian 03 was carried out to determine the adsorption energy of these cations on protonated platinum cluster surface. Higher adsorption energy reflects more cation adsorption on the Pt surface. The higher adsorption energy also implies that many of a particular cation species are occupying the surface of the Pt catalyst. The calculations showed that [EMIm]<sup>+</sup> exhibited the highest adsorption energy of 249 kJ mol<sup>-1</sup> followed by [Epdy]<sup>+</sup> (200 kJ mol<sup>-1</sup>) and [N1114]<sup>+</sup> that exhibited only 7.5 kJ mol<sup>-1</sup>. Hence the electrochemical active surface area was reduced by the [EMIm]<sup>+</sup> IL molecules compared to [N1114]<sup>+</sup> and [Epdy]<sup>+</sup> ILs. These results explain why fuel cell performance with [N1114]<sup>+</sup> was higher than that with [Epdy]<sup>+</sup> and [EMIm]<sup>+</sup> ILs.

Graphite oxide (GO) has been successfully functionalized using 3-aminopropyltriethoxysilane IL [52]. The functionalized GO was used in high temperature PEMFCs as an additive in a polybenzimidazole (PBI) anion exchange membrane (AEM). The composite membrane had H<sup>+</sup> conductivity of 3.5 and 2.5 S m<sup>-1</sup> at 418 K for 3.5 and 2.0 per repeat units of PBI when imbibed with low concentrations of phosphoric acid (PA). The acidic groups in the 3-aminopropyltriethoxysilane IL functionalized GO such as carboxyl and epoxy oxygen groups, could facilitate proton hopping. This enables the membrane to be used in PEMFC. The functionalized ILGO has enhanced the H<sup>+</sup> conduction even with low PA loading. The ILGO performance in enhancing the PA imbibed PBI conductivity signaled its suitability for use in PEMFC. The ILGO bonds with H<sub>3</sub>PO<sub>4</sub> and provides pathways for fast H<sup>+</sup> transport. Hence, the ILGO is able to enhance conductivity without requiring high PA loading. This indicates that the ILGO-PBI film has potential for application in fuel cells. When tested in PEMFC, the ILGO-PBI-PA membranes showed overwhelming performance over a PBI-PA membrane. The MPDs of the fuel cells employing PBI and ILGO-PBI with the oxygen group located in GO were 2.6 W m<sup>-2</sup> and 3.2 W m<sup>-2</sup> with the higher MPD for 3.5 per repeat unit. The enhanced performance has been attributed to the higher H<sup>+</sup> conductivity.

Fang et al. [53] have copolymerized [VMI]I and [VBI]Br with styrene for alkaline fuel cell (AFC) application. The ionic conductivity of these [VBI]Br:styrene and [VMI]I:styrene AEM was 2.26 S m<sup>-1</sup> and 1.32 S m<sup>-1</sup> at 303 K, respectively. The water uptake and ion exchange capacity are 56.8% and 1.26 mmol g<sup>-1</sup>, respectively. The membrane was chemically stable even after treatment in high NaOH concentrations at 333 K for 120 h. The H<sub>2</sub>/O<sub>2</sub> fuel cell with [VBI]Br:styrene of molar ratio 10:18 exhibited V<sub>oc</sub> of 1.07 V. The MPD of the H<sub>2</sub>/O<sub>2</sub> fuel cell was 1160 W m<sup>-2</sup> at J<sub>sc</sub> of 2300 A m<sup>-2</sup> at 333 K. These results demonstrate bright prospect of AEMs for AFC.

Novel OH<sup>-</sup> AEMs with IL consisting of butanediyl-1,4-bis(N-dodecylimidazole bromide) cation has been synthesized for AFC [54]. The anionic conductivity of the electrolyte film reached 4.19 S m<sup>-1</sup> at 353 K. This work showed that AEMs based on imidazolium cations have potential for application in AFCs.

Ortiz-Martínez et al. [55] have embedded a polymer-IL membrane into a carbon cathode for application in microbial fuel cells (MFCs). The IL was methyltrioctylammonium chloride. The MFC works when organic matter is oxidized by microbes and the electrons produced are transferred to the carbon cathode. The cell achieved a volumetric MPD of  $0.613 \text{ W m}^{-3}$ , which is about 10 times higher than the output of typical membranes. Coulombic efficiency also increased from 19.18 to 64.96%. The results obtained by these researchers indicate the potential application of embedded polymer IL membrane-cathode assembly in MFCs. This approach also improved contact between the separator and cathode.

SILMs also have potential for use in MFCs as proton exchange membranes. SILMs have been evaluated by Hernández-Fernández et al. [56]. The ILs used were [BMIM<sup>+</sup>] and [OMIM<sup>+</sup>] and [MTOA<sup>+</sup>] cation combined with Cl<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup> and TFSI<sup>-</sup> anions. The voltage of the MFC with different SILMs was monitored continuously for more than 160 h. The fuel cell using the supported [OMIM<sup>+</sup>][PF<sub>6</sub><sup>-</sup>] film attained the highest voltage of ~0.14 V. It is unfortunate that the IL in the film has the highest toxicity. The highest chemical oxygen demand (COD) removal for the MFCs has been achieved using [MTOA<sup>+</sup>][Cl<sup>-</sup>]. Its value was 89.1%. Its noncotoxicity is comparable to the commercial membranes such as Ultrex<sup>®</sup> and Nafion<sup>®</sup> with 88.3% and 90.7%, respectively.

In another study Ref. [57] [MTOA<sup>+</sup>][Cl<sup>-</sup>], [OMIM<sup>+</sup>][PF<sub>6</sub><sup>-</sup>], [P4,4,4,1<sup>+</sup>][MeSO<sub>4</sub><sup>-</sup>] and [P4,4,4,1<sup>+</sup>][TOS<sup>-</sup>] IL-based membranes were evaluated. The highest COD removal value was still achieved by the [MTOA<sup>+</sup>][Cl<sup>-</sup>]-based membrane while the [P4,4,4,1<sup>+</sup>][TOS<sup>-</sup>] and Nafion<sup>®</sup>117 membranes exhibited slightly lower CODs. In terms of volumetric power density (VPD), [P4,4,4,1<sup>+</sup>][TOS<sup>-</sup>] membrane offered higher VPD ( $0.795 \text{ W m}^{-3}$ ) compared to Nafion<sup>®</sup>117 ( $0.756 \text{ W m}^{-3}$ ). The fuel cell based on [MTOA<sup>+</sup>][Cl<sup>-</sup>] membrane exhibited  $0.237 \text{ W m}^{-3}$ . Overall performance among the ILs applied, [P4,4,4,1<sup>+</sup>][TOS<sup>-</sup>] showed better performance than Nafion<sup>®</sup>117 in terms of VPD and COD removal.

## 5. IL in lithium batteries

Due to their high energy density, lithium ion batteries (LIBs) have become attractive power sources for many applications such as mobiles, cameras and laptops. The specific energy in  $\text{Wh kg}^{-1}$  that can be delivered by LIBs, Ni-MH, Ni-Cd and lead acid batteries is 160, 90, 45 and 40, respectively. Hence lead acid batteries can only deliver 25% of the energy that can be supplied by LIBs.

Li et al. [58] have prepared a novel CPE with a PIL, namely, poly((4-vinylbenzyl) trimethylammonium bis(trifluoromethanesulfonyl)imide) as the host, DEME-TFSI ionic liquid, LiTFSI salt and nanosilica filler. PIL-based electrolytes with IL could effectively improve the electrode/electrolyte interface, which signaled a direction for the application of PIL electrolytes in LIBs. The compatible PIL-IL combination provides stable PEs with minimized phase separation and leakage. The electrical conductivity increased with IL content attributed to the increased amorphousness brought about by the plasticizing effect of DEME-TFSI. At 60% IL content, the electrolyte conductivity was  $7.58 \times 10^{-2} \text{ S m}^{-1}$  at 333 K. The

assembled Li/PIL-IL-LiTFSI-SiO<sub>2</sub>/LiFePO<sub>4</sub> cell showed that the IL was able to penetrate into the electrode and exhibited discharge capacity of ~136 Ah kg<sup>-1</sup> at 0.1 C. The cell recorded capacity fading of 0.075 Ah kg<sup>-1</sup> per cycle for 40 cycles. The specific discharge capacity of the cell was still 134 Ah kg<sup>-1</sup> even after 50 cycles.

ILGPE has been prepared by photocuring a mixture containing MPPipTFSI ionic liquid, LiTFSI and ethoxylated bisphenol A diacrylate, a long chain monomer [59]. MPPipTFSI had a sufficiently high conductivity to be applied in electrochemical devices and its wide voltage stability (5.8 V versus Fc/Fc<sup>+</sup>) provided good compatibility with the LiFePO<sub>4</sub> cathode. The IL-GPE conductivity was  $6.4 \times 10^{-3}$  S m<sup>-1</sup> at 298 K and increased with temperature to 0.48 S m<sup>-1</sup> at 368 K. The IL-GPE electrochemical stability was ~4.8 V versus Li/Li<sup>+</sup>. The cell Li/IL-GPE/LiFePO<sub>4</sub> displayed stable cyclability with capacity that is 4% less than the LiFePO<sub>4</sub> theoretical capacity at C/20 rate and 298 K. This showed that the IL-GPE provides good electrode/electrolyte interfacial contact and is a promising electrolyte for flexible LIBs.

A SPE system comprising PVdF host, an ionic liquid MePrPipNTf<sub>2</sub>, LiTFSI salt and VC have been prepared by Swiderska-Mocek [60]. VC is an additive to help form the solid electrolyte interphase (SEI) layer. The conductivity of the elastic membrane was 0.44 S m<sup>-1</sup> at 298 K. The activation energy was 12.4 kJ mol<sup>-1</sup>. The IL-incorporated membrane decomposed at 583 K. The high decomposition temperature signaled the safe use of the membrane in lithium polymer batteries at elevated temperatures. The Li<sup>+</sup> cell with the quaternary electrolyte PVdF + LiTFSI + MePrPipNTf<sub>2</sub> + VC can display good cyclability and safely deliver high specific capacities with LiFePO<sub>4</sub> cathode. The researchers also used LiMn<sub>2</sub>O<sub>4</sub> in place of LiFePO<sub>4</sub> [61]. The LiMn<sub>2</sub>O<sub>4</sub> cathode also exhibited good specific capacity. The full LiMn<sub>2</sub>O<sub>4</sub>/quaternary PE/Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> cell displayed good cycling performance indicating that the PE can also be safely used with LiMn<sub>2</sub>O<sub>4</sub> as cathode in LIBs.

Yang et al. [62] have used poly(VdF-co-HFP)-based GPEs with LiTFSI salt and B<sub>4</sub>MePyTFSI for application in LIB. The ILGPE 66.7 wt. % (PVdF-HFP/LiTFSI)-33.3 wt. % B<sub>4</sub>MePyTFSI exhibited a maximum Li<sup>+</sup> ionic conductivity of 0.20 S m<sup>-1</sup>. The Li/ILGPE/LiFePO<sub>4</sub> cell showed high capacity and good cyclability.

The ionic liquid BMImBF<sub>4</sub> was introduced into PVDF-HFP/PMMA-LiClO<sub>4</sub> blend membrane [63]. The GPE was microporous. After addition of IL into the microporous GPE, T<sub>g</sub> was observed to decrease. However the IL uptake into the membrane increased. The reason was that the IL that interacted with the polymer disrupted some of the PVDF-HFP crystalline phases and increased amorphousness that decreased T<sub>g</sub> of the GPE. The addition of LiClO<sub>4</sub> also helped to expand the amorphous zone. The LiFePO<sub>4</sub>/GPE/Li coin-type cell exhibited good cyclability.

PIL-plastic crystal CPE consisting of P(DADMA)TFSI PIL, succinonitrile (SN) and LiTFSI as the Li<sup>+</sup> ion source [64]. The 40%PIL-40%SN-20%LiTFSI (designated as 50% SN) electrolyte exhibited a high ambient conductivity, a wide potential window and good mechanical strength. The Li/50% SN/LiFePO<sub>4</sub> cell discharged at C/10 rate delivered a capacity of ~150 Ah kg<sup>-1</sup> at 298 K and has good capacity retention. The findings illustrated the fact that the electrolyte has great potential in LIBs.



## 6. IL in supercapacitors

The application of supercapacitors for energy storage can help to minimize dependence on fossil fuels. According to Mysyk et al. [65], supercapacitors have energy density higher than electrolytic capacitors. They also have power density higher than rechargeable batteries. Supercapacitors bridge the gap between electrolytic capacitors and rechargeable batteries. Supercapacitors can be divided into three general classes. There are electrical double layer capacitors (EDLCs), pseudocapacitors and hybrid capacitors. Each class is characterized by its charge storage mechanism. These mechanisms are non-Faradaic, Faradaic and a combination of both. Non-Faradaic mechanism can be likened to electrostatic charge storage. Faradaic reaction is a heterogeneous charge transfer reaction that occurs on the surface of an electrode.

Supercapacitors comprise an anode, electrolyte and a cathode [66]. The potential stability window of the electrolyte determines the supercapacitor voltage. The electrode and electrolyte also determine the power density and cyclability of the supercapacitor. Hence, it is important to choose the proper electrolyte [67].

A lot of attention has been given to carbon-based capacitors. This is because these carbonaceous materials possess diversified morphologies, excellent cycling stability, high power capability and conductivity [68, 69]. EMImBF<sub>4</sub> was introduced as an ion conducting medium in an EDLC of AC nanofibers. Propylene carbonate (PC) that can dissolve EMImBF<sub>4</sub> was also added into the electrolyte. Without PC, the EDLC delivered a decreasing capacitance from ~78 to ~60 F g<sup>-1</sup>. On addition of PC, the capacitance delivered maintained at ~80 F g<sup>-1</sup>. This showed that PC helped to recover the lost capacitance by breaking the interaction between the carbon micropore wall and EMIm<sup>+</sup> cation and also releasing the immobile ions in the micropores during the cycling. By incorporating Cu(II) into EMImBF<sub>4</sub> [70], the electrochemical capacitors exhibited good stability with only ~9% capacitance loss after 500 cycles. The capacitance is higher than that obtained from an EDLC using pure EMImBF<sub>4</sub> as electrolyte. The average specific capacitance is 108 F g<sup>-1</sup> for EMImBF<sub>4</sub> and 225 F g<sup>-1</sup> for EMImBF<sub>4</sub> with Cu(II). The increase indicated that the Faradaic pseudocapacitance associated with the Cu species has contributed considerably to the total capacitance of the EDLC.

The ionic liquid DEME-BF<sub>4</sub> with wide potential window of 6 V also showed high potential for electrochemical capacitors. Its conductivity at 25°C is considerably high, 4.8 mS cm<sup>-1</sup> [71]. Aliphatic quaternary ammonium-based ILs are expected to show higher cathodic stability since its melting point is higher compared to aromatic ILs. EDLC with showed little gas release and smaller capacity fade at 373 K. This implies that AC electrodes and DEME-BF<sub>4</sub> electrolyte combination contributed to cell stability compared to the EDLC using TEA-BF<sub>4</sub>/PC, which exhibited a large capacity fade at 373 K. The DEME-BF<sub>4</sub> EDLC retained 85% of its initial capacity even after 500 cycles.

According to Yuyama et al. [72], ILs with BF<sub>4</sub><sup>-</sup> anion exhibited better stability and performance compared to PF<sub>6</sub><sup>-</sup> and TFSI<sup>-</sup> anions when used in EDLCs. The equivalent series resistance (ESR) and direct current (dc) resistance at 298 K and 243 K decreased accordingly as TFSI<sup>-</sup> > PF<sub>6</sub><sup>-</sup> > BF<sub>4</sub><sup>-</sup>. According to Fletcher et al. [69], dc resistance and ESR decreased with increasing temperature and this can be accredited to the decreasing IL electrolyte viscosity.



Decrease in viscosity led to the increase in anion and cation self-diffusion. This implied that ion dissociation and ionic mobility have increased at elevated temperatures.

A carbon-based supercapacitor has been fabricated using protic ionic liquid (PrIL) as novel electrolyte [65]. PrILs are created when one proton is transferred between a Brönsted acid and base. When compared to aprotic ILs, PrILs are cheaper and easier to synthesize [73]. Cyclic voltammograms of PrILs exhibit reversible redox peaks. This indicated pseudo-Faradaic charge transfer. Oxidative  $\text{HNO}_3$  treatment of AC augmented surface performance and resulted in enhanced capacitance that is attributed to pseudo-Faradaic contribution. PrIL-based capacitors show a wider potential window than capacitors using aqueous  $\text{H}_2\text{SO}_4$ . AC-PrIL combination shows promise for supercapacitors with good energy characteristics.  $\text{Et}_3\text{HTFSI}$  PrIL has been used as an ion conducting medium in supercapacitors with AC electrodes [74]. Supercapacitors with less than 200 ppm of  $\text{H}_2\text{O}$  in  $\text{NEt}_3\text{H TFSI}$  electrolyte are able to operate at 2.5 V. At water concentration of 200 ppm the electrolyte was considered dry. The voltage of AC-PrIL-based supercapacitors will be affected if the electrolyte contains a significant amount of water. The cell voltage will then not be able to exceed 1.2 V, that is, the potential window of water. Brandt et. al [75] have studied various carbon-based supercapacitors using various PrILs such as  $\text{Et}_3\text{NHTFSI}$ ,  $\text{Me}_3\text{NHTFSI}$  and  $\text{PYRNO}_3$  as electrolytes for long-term cycling stability. They reported that the supercapacitor employing PrIL-based supercapacitors exhibited stability even after 30,000 cycles. The supercapacitors can also perform over wide temperature range. The PC- $\text{Me}_3\text{NHTFSI}$  mixed electrolyte can be used even at temperatures down to 250 K. The supercapacitor containing the protic IL  $\text{Et}_3\text{NHTFSI}$  showed stable performance from 283 to 333 K.

Timperman et al. [67] have described the use of eutectic PrIL mixtures of  $\text{PYRNO}_3$  and  $\text{PYRTFSI}$  as ion conducting medium for application in AC-based supercapacitors. The capacitors showed good capacity retention. Using electrolyte with  $[\text{PYR}]/[\text{NO}_3]$  ratio of 0.72 at 298 K, the capacitor showed more than 95% efficiency at 1.5 V for at least 80 h and at 2.0 V for 110 h.

The performance of IL electrolytes consisting of various cations such as  $\text{EMIm}^+$  and  $\text{BMP}^+$  and  $\text{TFSI}^-$ ,  $\text{BF}_4^-$  and  $\text{DCA}^-$  anions have been investigated [76].  $\text{BMP-DCA}$  ionic liquid showed excellent electrolyte behavior for supercapacitor with graphene nanosheet (GNS) electrodes. The supercapacitor delivered  $235 \text{ F g}^{-1}$  specific capacitance, energy density of  $88 \text{ Wh kg}^{-1}$  and specific power  $17.5 \text{ kW kg}^{-1}$  at 298 K. IL electrolytes perform better at high temperatures. This is because their conductivity increased with temperature and their viscosity decreased. The decrease in viscosity led to enhancement in ionic mobility. This led to increased conductivity. Stability was also maintained at elevated temperatures.

One of the challenges facing IL supercapacitors is to improve electrolyte accessibility to the nanocarbon surface. According to Trigueiro et al. [77], the wettability of the electrodes with an IL electrolyte can be facilitated by the poly(IL) molecules electrostatically linked to reduced graphene oxide (RGO) surface electrode, producing high specific capacitance. As an example, a  $[\text{MPPy}][\text{TFSI}]$ -modified RGO electrode (PIL:RGO) exhibited a drop in specific capacitance of only 20% as scan rate increased from 10 to  $30 \text{ mV s}^{-1}$  at 298 K, while an RGO capacitor lost 42% of its specific capacitance under similar conditions. The effective intercalation and distribution of the poly(IL) molecules in the RGO nanosheets contributed to the improved

wettability as well as interaction with the IL. These results implied that 80% capacity is retained for PIL:RGO and 58% RGO capacitors. At 333 K, 70% of the capacity was retained for PIL:RGO and 61% capacity retention for RGO-based supercapacitors.

Another approach to obtain stable polymer electrolytes thermally and electrochemically is by incorporating RTIL into polymer electrolytes [78]. Pandey et. al [79] has compared the EDLC performance using electrolyte in the solid-state and ionic liquid incorporated polymer electrolytes. The electrodes of EDLCs comprised multiwalled carbon nanotube (MWCNT). The polymer electrolytes consisted of PEO, triflate salts of magnesium and lithium and EMImTf ionic liquid. The ambient conductivity was  $\sim 10^{-2} \text{ S m}^{-1}$ . The addition of IL increased the polymer backbone flexibility and enhanced segmental motion. The use of the triflate salts and IL introduced  $\text{Li}^+/\text{Mg}^{2+}$ ,  $\text{EMIm}^+$  and  $\text{CF}_3\text{SO}_3^-$  free ions. The presence of many types of mobile ionic species increased the possibility of formation of more double layers where energy was stored. The enhanced flexibility is also useful for proper electrode-electrolyte contact. Incorporating EMImTf resulted in a substantial increment of PEO-Mg(Tf)<sub>2</sub> electrolyte conductivity. MWCNT with Li-based and Mg-based electrolyte could deliver between 1.7 and 2.1  $\text{F g}^{-1}$  and between 2.6 and 3.0  $\text{F g}^{-1}$ , specific capacitance, respectively. Without IL incorporation the capacitance per unit mass were  $\sim 0.03 \text{ F g}^{-1}$  and  $\sim 0.01 \text{ F g}^{-1}$  for the Mg- and Li-system, respectively. This showed IL contribution on EDLC capacitance.

Ayalneh Tiruye et al. [78] have assembled supercapacitors containing two parts of a pyrrolidinium-based PIL, that is, pDADMTFSI and three parts  $\text{PYR}_{14}\text{TFSI}$  ionic liquid. A supercapacitor with PIL-based PE delivered specific capacitance and specific energy of 100  $\text{F g}^{-1}$  and 32  $\text{Wh kg}^{-1}$ , respectively. At 333 K, specific energy increased to 42  $\text{Wh kg}^{-1}$  at discharge current density 1  $\text{mA cm}^{-2}$ . These values are a little less than that using pristine  $\text{PYR}_{14}\text{TFS}$ , but are higher than that of supercapacitors using conventional polymer electrolytes. The IL-based polymer electrolytes have a wide potential window that allowed operation of the all solid-state supercapacitors at voltages of 3.5 V.

The addition of BmImCl into the  $\text{PVA}/\text{CH}_3\text{COONH}_4$  electrolyte enhanced the ionic conductivity due to its strong plasticizing effect, environmental friendly nature and high ion content [80]. In the presence of IL, the polymer chains become more flexible, thus the polymer segmental motion increased. This assisted ionic transport that conferred the high ionic conductivity. This result agreed with the differential scanning calorimetric (DSC) analysis as subambient  $T_g$  was observed on addition of IL. At these sub-ambient temperatures, the polymer electrolyte is in the rubbery state as the surrounding temperature is much higher than  $T_g$ . The molecules in the polymer matrix are allowed to undergo orientation and conformational changes in the rubbery phase. Moreover, the physicochemistry of IL such as viscosity and dielectric constant also contribute to ionic conductivity enhancement. EDLC fabricated with the most conducting ion conducting polymer can be charged up to 4.8 V. By doping IL into the polymer electrolyte also increased the capacitive nature of EDLC as the specific capacitance of 28.36  $\text{F g}^{-1}$  was achieved. The inclusion of IL not only improved the electrode-electrolyte interfacial contact, but also improved the electrolyte and EDLC properties. Therefore, this is also a good prospect for improving the electrochemical performance of an EDLC.

The ionic liquid, BmImBr has been introduced into a PVA/CH<sub>3</sub>COONH<sub>4</sub> PE system for application in EDLC [81]. The EDLC delivered a capacitance of 21.89 F g<sup>-1</sup> and continued to do so for 250 cycles.

An electrical conductivity of 0.73 S m<sup>-1</sup> was achieved at 393 K upon adulteration of 50 wt. % BmImCl to the PVA/CH<sub>3</sub>COONH<sub>4</sub> PE system [80]. This is accompanied with the lowering of T<sub>g</sub>. The primary cause of reduction in T<sub>g</sub> was the ability of the IL to plasticize. Plasticization softened the polymer backbone, increased segmental motion thus helped in facilitating ionic transport. On addition of the IL containing ion conducting medium, the amorphousness of the membrane was observed to increase. It was also observed that the polymer electrolyte exhibited a wider potential stability range. The presence of IL has also improved the electrochemical behavior of the EDLC delivering 2.39 Wh kg<sup>-1</sup> of specific energy and 19.79 W kg<sup>-1</sup> of specific power with Coulombic efficiency above 90%. The specific capacitance of 28.36 F g<sup>-1</sup> was obtained with better electrochemical characteristics.

Addition of BMImTf ionic liquid in PVA/CH<sub>3</sub>COONH<sub>4</sub> PE system [82] resulted in the polymer electrolyte exhibiting strong adhesive properties. Thus, better electrode-electrolyte interfacial contact can be provided. The specific capacitance of the EDLC obtained was 2.02 from 0.14 F g<sup>-1</sup> without IL. This implied that the IL-based polymer electrolytes possessed higher dielectric constant compared to the IL-free polymer electrolyte. The addition of IL has also extended the electrolyte voltage window and improved thermal stability.

The BdMImBF<sub>4</sub> ionic liquid was added into a gel matrix that comprised a blended host of PVP/PVdF-HFP and magnesium triflate salt. The gel was used in an EDLC [83]. The interaction between the IL and the polar groups of the polymer chain increased amorphousness of the GPE. The ionic conductivity achieved a maximum value of 0.29 S m<sup>-1</sup> after 7.5 wt. % of BdMImBF<sub>4</sub> was added. The calculated specific energy and power were 14 Wh kg<sup>-1</sup> and 21 W kg<sup>-1</sup>, respectively.

## 7. Summary

ILs consist of poorly coordinating cations and anions and are molten salts at room temperature. They have high thermal stability, wide potential window and high electrical conductivity. ILs are green solvents with negligible vapor pressure. IL such as EMImTf, EMImBF<sub>4</sub> and PP<sub>24</sub>TFSI, to name a few can enhance ionic conductivity when added to PEs. Conductivity enhancement is attributed to the additional ions supplied by the IL, the plasticizing nature of the IL and its low viscosity that facilitates ion mobility. The plasticizing nature of ILs softens the polymer backbone resulting in the increase in polymer segmental motion. This implies that IL can increase amorphousness of a PE. ILs with short alkyl chains are less viscous and hence suitable for facilitating ion mobility. However, IL containing Im<sup>+</sup> cation with long alkyl chain length can delay electron recombination, enhance J<sub>sc</sub> and improves IPCE in DSSCs. EMImTFSI, EMImTf and EMImDCN are low viscosity ILs that are able to increase ionic conductivity of and PEO:NaI:I<sub>2</sub> systems. It is also to be noted that most sulfonium ion-based ILs have higher conductivity than ammonium ion-based ILs due to the lower viscosity of the

former. Incorporation of ILs, for example, BMImTf can increase thermal stability of a PE such as in 49 wt. % PEMA-21 wt. % (PVdF-HFP)-30 wt. % LiTf sample. DMPImI is an ionic liquid that has been added to a PEO-PEG-KI system to produce an  $I_2$ -free GPE that was able to reduce electron recombination and dark current in a DSSC. Imidazolium type aprotic IL when added into sulfonated poly (ether ketone) or SPEK not only increased ionic conductivity, but also enabled the membrane to operate under anhydrous condition between at elevated temperatures. The ability of the membrane to operate at 413 K shows its potential as a candidate for PEMFC. The MePrPipNTf<sub>2</sub> incorporated into a PVdF + LiTFSI + VC electrolyte system decomposed at a high temperature of ~583K. This signaled the safe use of the membrane in lithium polymer batteries at elevated temperatures. The ILGPE 66.7 wt. % (PVdF-HFP/LiTFSI)-33.3 wt. % B<sub>4</sub>MePyTFSI exhibited a maximum Li<sup>+</sup> ionic conductivity of 0.20 S m<sup>-1</sup>. The Li/ILGPE/LiFePO<sub>4</sub> cell showed high capacity and good cyclability. The addition of BmImCl to the PVA/CH<sub>3</sub>COONH<sub>4</sub> PE system is accompanied with the lowering of T<sub>g</sub>, wider potential stability range and improved EDLC electrochemical behavior.

## Abbreviations

[C <sub>2</sub> mim][C <sub>n</sub> SO <sub>3</sub> ]	1-Ethyl-3-methylimidazolium sulfonate; (subscript n had values n = 1, 2, 4 as methanesulfonate, ethanesulfonate and butanesulfonate, respectively)
[C <sub>2</sub> mim][C <sub>n</sub> SO <sub>4</sub> ]	1-Ethyl-3-methylimidazolium sulfate (subscript n had values n = 1, 2 as methanesulfonate and ethanesulfonate, respectively)
[C <sub>2</sub> mim][diC <sub>n</sub> PO <sub>4</sub> ]	1-Ethyl-3-methylimidazolium phosphate (subscript n had values n = 1, 2 as dimethanephosphate and diethanephosphate, respectively)
[EmIm]HSO <sub>4</sub>	Ethylmethyl imidazolium hydrosulfate
[Epyd]HSO <sub>4</sub>	Ethyl pyridinium hydrosulphate
[MPPy][TFSI]	Poly(1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide)
[MTOA <sup>+</sup> ]	Methyl trioctylammonium cation
[MTOA <sup>+</sup> ][Cl <sup>-</sup> ]	Methyl trioctyl ammonium chloride
[N1114] <sup>+</sup>	Trimethylethyl amide cation
[N1114]HSO <sub>4</sub>	Trimethylethyl amide hydrosulphate
[OMIM <sup>+</sup> ][PF <sub>6</sub> <sup>-</sup> ]	1-Octyl-3-methylimidazolium hexafluorophosphate
[P4,4,4,1 <sup>+</sup> ][TOS <sup>-</sup> ]	Triisobutyl(methyl)phosphonium tosylate,
[P4,4,4,1 <sup>+</sup> ][MeSO <sub>4</sub> <sup>-</sup> ]	Tributylmethyl phosphonium methylsulfate
[VBI]Br	1-Vinyl-3-butyliimidazolium bromide
[VMI]I	1-Vinyl-3-methylimidazolium iodide
AC	Activated carbon
AFC	Alkaline fuel cell
B <sub>4</sub> MePyTFSI	1-Butyl-4-methylpyridinium bis(trifluoromethanesulfonyl)imide
BdMImBF <sub>4</sub>	1-Butyl-2,3-dimethylimidazolium tetrafluoroborate

$\text{BF}_4^-$	Tetrafluoroborate anion
$\text{BMImBF}_4$	1-Butyl-3-methylimidazolium tetrafluoroborate
$\text{BmImBr}$	1-Butyl-3-methylimidazolium bromide
$\text{BMImCl}$	1-Butyl-3-methylimidazolium chloride
$\text{BMImI}$	1-Butyl-3-methylimidazolium iodide
$\text{BMImNO}_3$	1-Butyl-3-methylimidazolium nitrate
$\text{BMImPF}_6$	1-Butyl-3-methylimidazolium hexafluorophosphate
$\text{BMImTf}$	1-Butyl-3-methylimidazolium trifluoromethanesulfonate
$\text{BMP}^+$	N-Butyl-N-methylpyrrolidinium cation
$\text{C}_{18}\text{H}_{36}\text{O}_3$	12-Hydroxystearic acid
CPE	Composite polymer electrolyte
$\text{DCA}^-$	Dicyanamide anion
$\text{DEME-BF}_4$	N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium tetrafluoroborate
DEME-TFSI	N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis (trifluoromethanesulfonyl) imide
$\text{DMPImI}$	1,2-Dimethyl-3-propylimidazolium iodide
DSSC	Dye-sensitized solar cell
EMiDCA	1-Ethyl-3-methyl dicyanamide
$\text{EMIm}^+$	1-Ethyl-3-methylimidazolium cation
$\text{EMImBF}_4$	1-Ethyl-3-methylimidazolium tetrafluoroborate
$\text{EMImDCN}$	1-Ethyl-3-methylimidazolium dicyanamide
$\text{EMImI}$	1-Ethyl-3-methylimidazolium iodide
$\text{EMImTf}$	1-Ethyl-3-methylimidazolium trifluoromethanesulfonate
$\text{EMImTFSI}$	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
$\text{Epdy}^+$	Ethyl pyridinium cation
$\text{Et}_3\text{NHTFSI}$	Triethylammonium bis(tetrafluoromethylsulfonyl)imide
FF	Fill factor
GPE	Gel polymer electrolyte
$\text{GuSCN}$	Guanidine thiocyanate
IL	Ionic liquid
ILGE	Ionic liquid gel electrolyte
ILGO	Ionic liquid graphite oxide
IPCE	Incident photon-to-electron conversion efficiency
$J_{\text{sc}}$	Short-circuit current density
LGPE	Ionic liquid gel polymer electrolyte
$\text{LiPF}_6$	Lithium hexafluorophosphate
$\text{LiTf}$	Lithium trifluoromethanesulfonate



LiTFSI	Lithium bis(tetrafluoromethylsulfonyl)imide
$\text{Li}_4\text{Ti}_5\text{O}_{12}$	Spinel lithium titanate
MBImI	1-Methyl-3-butylimidazolium iodide
$\text{Me}_3\text{NHTFSI}$	Trimethylammonium bis(tetrafluoromethylsulfonyl)imide
MEMP- $\text{BF}_4$	N-(2-methoxyethyl)-N-methylpyrrolidinium
MePrPip <sup>+</sup>	N-methyl-N-propylpiperidinium cation
MePrPipNTf <sub>2</sub>	N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide
MHImI	1-Methyl-3-hexylimidazolium iodide
MPD	Maximum power density
MPImI	1-Methyl-3-propylimidazolium iodide
MPPipTFSI	N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide
N-MBI	N-methylbenzimidazole
NTf <sub>2</sub> <sup>-</sup>	Bis(trifluoromethanesulfonyl)imide anion
P[VP-co-VAc]	Poly[1-vinylpyrrolidone-co-vinyl acetate]
PAN	Polyacrylonitrile
PBI	Polybenzimidazole
pDADMTFSI	Poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl)imide
PE	Polymer electrolyte
PEDOT-NF	Poly(3,4-ethylenedioxythiophene) nanofibers
PEG	Polyethylene glycol
PEMA	Poly(ethyl methacrylate)
PEMFC	Proton exchange membrane fuel cells
PEO	Poly(ethylene oxide)
PIL	Polymeric ionic liquid
PMAPII	Poly(1-methyl 3-(2-acryloyloxypropyl) imidazolium iodide)
Poly(AA/CTAB)	Poly(acrylic acid/cetyltrimethylammonium bromide)
Poly(AA/GR)	Poly(acrylic acid/gelatin)
Poly(HEMA/GR)	Poly(hydroxyethyl methacrylate/glycerol)
PP <sub>24</sub> TFSI	N-butyl-N-ethylpiperidinium N,N-bis(trifluoromethane)sulfonimide
Pr <sub>4</sub> NI	Tetrapropyl ammonium iodide
PrIL	Protic ionic liquid
PVA	Polyvinyl alcohol
PVdF-HFP	Poly(vinylidene fluoride-co-hexafluoropropylene)
PVP/PVdF-HFP	Poly(vinyl pyrrolidone)/poly(vinylidene fluoride-co-hexafluoropropylene)

PMMA	Poly(methyl methacrylate)
PYR <sub>14</sub> TFSI	(N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide)
PYRNO <sub>3</sub>	Pyrrolidinium nitrate
PYRTFSI	Pyrrolidinium bis(trifluoromethanesulfonyl)imide
RT	Room temperature
RTIL	Room temperature ionic liquid
SILM	Supported IL membrane
SPE	Solid polymer electrolyte
SPEK	Sulfonated poly (ether ketone)
TBP	Tert-butylpyridine
TEA-BF <sub>4</sub> /PC	Tetraethylammonium tetrafluoroborate/propylene carbonate
TFSI <sup>-</sup>	Bis(trifluoromethylsulfonyl)imide anion
T <sub>g</sub>	Glass transition temperature
TIPIL	Three-armed imidazolium phenoxy ionic liquid
VC	Vinylene carbonate
V <sub>oc</sub>	Open circuit voltage

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