# Chapter 1
# Organic–Inorganic Membranes Impregnated with Ionic Liquid

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**Abstract** The use of ionic liquids (ILs) as fuel cell electrolytes is gaining growing interest. Their application as fuel cell membranes is fairly recent but much progress has been made in this field. Solid or semisolid conductive electrolytes are generally preferred over fluidic materials in these devices, and ILs have shown great potential to fabricate polymer membranes with good mechanical properties and high conductivity. Thus, they could replace conventional perfluorosulfonic acid membranes for operation at low and high temperatures. This chapter focuses on the recent advances in the application of ionic liquid-based polymer membranes for the development of fuel cell technology. Although special attention is paid to proton exchange membranes fuel cells (PEMFCs), other fuel cell types such as alkaline (AFCs) and microbial fuel cells (MFCs) are also covered. The membrane configurations comprised in this work include several ionic liquid–polymer membrane options such as supported and inclusion membranes, polymerizable ionic liquids and ionic liquid–polymer composites. The key factors affecting membrane performance in each case are discussed.

**Keywords** Fuel cell · Proton exchange · Ion exchange · Electrolyte · Ionic liquid · Polymer membrane

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# 1 Introduction

Fuel cells are a promising technology for use as source of bioenergy from different types of low-cost materials such as air, methanol or even wastes. In recent years, many advances have been made in material science in order to develop novel and efficient membranes for their application in these devices. Among the most important factors in selecting a membrane for fuel cells are: (i) conductivity, (ii) internal resistance to ion transport, (iii) thermal, chemical and mechanical stability, (iv) biofouling trend, (v) fuel permeability and (vi) cost [1–3]. The efficiency of the separator is crucial for the widespread implementation of fuel cell technology. Perfluorosulfonic acid membranes such as Nafion, which are commonly used in fuel technology, present several limitations at high temperature and under anhydrous conditions in addition to being expensive. Since the operation of fuel cells at elevated temperature is receiving much attention because it can greatly enhance reaction kinetics at electrodes, other alternatives need to be found. The development of alternative membranes for low and room temperature fuel cells also poses a challenge in terms of durability and cost.

The current trend towards improving the performance of fuel cell technology includes the development of membranes based on ionic liquids (ILs). Their unique properties make possible to adapt this type of membranes to a specific device, since the chemical and physical properties of ionic liquids can be tailored by varying the nature of the cation and the anion in their structure [4]. Ionic liquids have attracted growing interest as electrolyte membrane due to their high conductivity and physical properties such as thermal stability.

The idea of including ionic liquids in fuel cell membranes is relatively recent and much progress is being made in this field. This chapter focuses on the recent advances in the field of polymer membranes based on ILs for their application in different types of fuel cells, mainly proton exchange membranes fuel cells (PEMFCs), but also other types such as alkaline (AFCs) and microbial fuel cells (MFCs). ILs can be used in their original state or in polymerized form as liquid phase or mixed with a polymer and other composite materials to form fuel cell membranes. All these options will be described in this chapter.

# 2 Ionic Liquids: General Properties and Applications

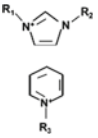
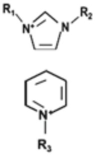
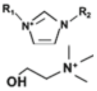
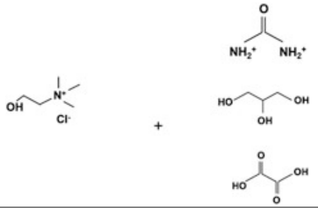
Ionic liquids have become one of the most promising materials investigated in the last decades for a broad range of chemical applications due their unique properties. These compounds are mixtures of anions and cations that remain liquid below 100 °C. They generally exhibit moderate polarities, high viscosities, negligible vapour pressure and virtually non-flammability. However, the main advantage of ILs is their task-specific functionality, since their properties can be easily adapted to a specific purpose by altering the substitutive group on the cation or the combined anion in their structure. These properties make them especially attractive for many technological applications, including electrochemical devices [5]. The synthesis of ionic liquids often involves the formation of the desired cation by several techniques such as amine protonation, with a subsequent anion exchange usually via the generation of a Lewis acid ionic liquid or by metathesis method [6].

Ethylammonium nitrate was the first ionic liquid reported in the literature by Walden [7] in 1914, however, it took nearly 70 years after that ILs started to gain much more importance. In 1982, dialkylimidazolium-based ionic liquids began to be deeply studied, especially ILs containing metal halide anions, such as chloroaluminate anions, which easily react with water [8]. Almost ten years later, these types of anions were replaced by halides such as tetrafluoroborate ($BF_4^-$) or hexafluorophosphate ($PF_6^-$). Dialkylimidazolium-based ILs often show moderate polarity and hydrophobic behaviour, and can be used as inert solvents [9–11]. Finally, a third generation of ionic liquids comprises those including biodegradable and low toxic cations and anions. They offer similar properties to those displayed by the ILs belonging to the second group but are generally more hydrophilic. This third group is usually characterized by the presence of cations such as choline and quaternary ammonium cations, and anions such as sugars, organic acids or alkylphosphates. This group also includes eutectic solvents, which consist of mixtures of salts (Table 1). The main advantage of third generation ionic liquids is the lower cost of the synthesis and purification processes, especially in the case of eutectic solvents [5, 12].

One of the most promising applications of ionic liquids is their use as green solvents, replacing polar organic solvents, which are volatile and therefore pose environmental risks. Instead, the vapour pressure of ionic liquids is near zero, enabling easy recovery and reusability. ILs have been used as replacement of volatile organic solvents in a wide variety of chemical processes, including separation and purification technology and reaction media in biochemical and chemical catalysis. Other major advantage is that there is a certain class of these compounds that does not denature enzymes and, therefore, are suitable for enzyme-based applications, such as enzymatic reactions or enzymatic fuel cells (EFCs). Ionic liquids have been employed as co-solvents with water, as a secondary phase in different types of mixtures and as non-aqueous solvents [13].

In recent years, ILs have been widely studied in immobilized form in several types of membranes for applications in separation technology and as ion exchange separators in fuel cells [14–17]. The application potential of ILs lies in their simple operation, possibilities for upscaled processes and environmental-friendly properties. IL membranes have been used as selective transport for several compounds such as organic acids, aromatic hydrocarbons, mixed gases and metal ions. They have also gained much attention for $CO_2$ capture [18]. Since ILs have high selectivity and ionic conductivity, including proton transport properties, separators based on these compounds have proven to offer promising prospects for fuel cell technology under several conditions, including anhydrous, non-anhydrous and alkaline conditions. For example, imidazolium-based ionic liquids have been used to prepare organic–inorganic hybrid alkaline anion exchange membranes (AEMs)

**Table 1** General classification of ionic liquids [5]

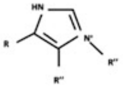
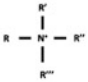
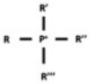
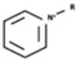
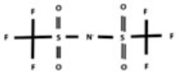
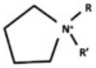
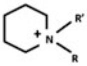
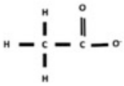
| Ionic liquid | Cations | Anions |
|---|---|---|
| First generation | <br>[R=Alkyl] | $AlCl_4^-$<br>$Al_2Cl_7^-$ |
| Second generation | <br>$NR_4^+$<br>[R=Alkyl] | $PF_6^-$<br>$BF_4^-$<br>$N(SO_2CF_3)_2^-$<br>$Me_2SO_3^-$ |
| Third generation | <br>Amino acids<br>[R= Oxygenated alkyl] | Amino acids<br>$R_2PO_4^-$<br>$ROSO_3^-$ |
|  | Eutectic solvents<br> |  |

that, in addition to good conductivity, have exhibited good mechanical properties and excellent stability [19]. Table 2 lists the most common cations and anions in ionic liquids.

## 3 Ionic Liquids as Electrolytes in Fuel Cells

In recent years, the application of ionic liquids as non-aqueous electrolytes in electrochemical systems has attracted much interest due to their unique properties. These compounds offer wide stability windows with high resistance for electrochemical reduction and oxidation processes besides negligible vapour pressure and non-flammability. Although the specific conductivities of ionic liquids are lower compared to those of conventional aqueous electrolytes solutions yet still provide fairly high conductivities depending on the anions and cations present in their structure, with similar values to those offered by inorganic electrolytes in aprotic organic solvents [20]. The conductivities of ionic liquids at room temperature range

**Table 2** Common IL cations and anions

| Cations | | Anions | |
|---|---|---|---|
| <br>Imidazolium | <br>Tetraalkylammonium | <br>Tetrafluoroborate | <br>Hexafluorophosphate |
| <br>Tetraalkylphophonium | <br>Pyridinium | $Cl^-$<br>Chloride | <br>Bis(trifluoromethylsulfonyl)imide |
| <br>Pyrrolidinium | <br>Piperidinium | <br>Triflate | <br>Acetate |

from 0.1 to 18 mS $cm^{-1}$. Ionic liquids based on the group imidazolium have been reported to display higher overall ionic conductivities compared to other cationic groups. For instance, ILs containing the cation 1-ethyl-3-methylimidazolium, [emim], present an average conductivity of about 10 mS $cm^{-1}$, while ILs containing cations based on the ammonium, pyrrolidinium, piperidinium and pyridinium groups typically show overall lower conductivities up to 5 mS $cm^{-1}$. Also, ILs with lower viscosities tend to have higher conductivities [21]. These compounds have a broad stability window typically from 2 to 6 V, the most common value being around 4.5 V. The electrochemical window is defined by the reduction of the organic cation and the oxidation of the anion [22]. Regarding electrochemical stability, ionic liquids including halide anions (e.g. $Cl^-$, $Br^-$) offer lower stability values between 2 and 3 V, while ionic liquids based on fluorine-containing anions such as bis(trifluoromethylsulfonyl)imide, [$Tf_2N^-$], show wider electrochemical window up to 6 V. ILs based on tetraalkylammonium cations also have enhanced stability above 4 V [21–23]. All these properties make ionic liquids ideal as electrolytes for many electrochemical applications including advanced batteries, dye sensitized solar cells, double layer capacitors, actuators, thermocells, water splitting technology and fuel cells [24].

Protic ionic liquids (PILs), which have a proton available for hydrogen bonding, offer great potential as fuel cell electrolytes operating at ambient or high temperatures. ILs as proton carriers allow acid or basic aqueous electrolytes to be avoided when the use of non-aqueous electrolytes is required. PILs can be easily synthesized through the combination of a Brønsted acid and a Brønsted base, being characterized by the proton transfer from the acid to the base and acting as proton acceptor and donor. This provides them with unique properties compared to the rest of ionic liquids. Brønsted acidic ionic liquids (BAILs), which are very close to PILs, are a special case since they can act either as protic or aprotic ILs depending on whether the available proton is on the cation or the anion [25]. The ILs diethylmethylammonium trifluoromethanesulfonate, [dema][TfO], and 1-methylimidazolium tetrafluoroborate, [hmim][$BF_4$], are examples of protic ionic liquids with cations based on ammonium and imidazolium groups, respectively. The advantage of using PILs as electrolytes for PEMFCs is that they can be operated at temperatures above 100 °C under anhydrous conditions, which is especially important to ensure good performance in high-temperature fuel cells, including operational fuel cell voltage and current output. From a practical point of view, ionic liquids have shown great potential to fabricate polymer membranes. In this sense, solid or semisolid conductive electrolytes with good mechanical properties are preferred over fluidic materials. The proton transport mechanism in PILs can be explained by the combination of the Grotthuss and vehicle mechanisms. While the first mechanism refers to the proton hopping between hydrogen bondings, vehicle mechanism involves diffusion and migration phenomena. The predominant conduction mechanism strongly depends on the composition of each ionic liquid [26].

Although protic ionic liquids are particularly relevant, aprotic ionic liquids have also been used in fuel cells since they can offer high overall ionic conductivity in comparison to protic ILs. Furthermore, aprotic ILs have been of interest for fuel cells whose operation may not depend exclusively on proton exchange but also on the transport of other ion species, as in the case of several types of microbial fuel cells. In fact, several types of separators apart from proton exchange membranes have been investigated for this technology, including cation exchange membranes (CEM) and anion exchange membranes (AEM) [3].

## 4 Ionic Liquid Polymer Membranes for Fuel Cells

Due to the unique properties of ionic liquids, mainly their high ionic conductivity and excellent thermal stability, these materials have been studied as possible substitute for Nafion membranes. Nafion is a solid polymer electrolyte widely used as proton-conducting material in fuel cells. It consists of a copolymer of tetrafluoroethylene (TFE) and sulfonyl fluoride vinyl ether. The TFE material provides the backbone system for the membrane that contains sulfonic acid pending groups ($–SO_3H$). As is widely known, Nafion displays featured properties for its application in fuel cell technology such as chemical stability and mechanical durability. Under favourable conditions, Nafion membranes can offer maximum proton conductivities ($\sigma$) in the order of 10 mS $cm^{-1}$ [27]. However, several disadvantages related to operational limitations and high cost are associated with Nafion. For instance, it requires complete hydration to ensure a good performance, with a significant loss of conductivity at relative humidity (RH) levels below 100% and at temperatures above 80 °C due to dehydration. This makes Nafion especially suitable for low temperature fuel cells (LTFCs) but poses a problem for the practical implementation of several other types of fuel cells that need to be operated at temperatures higher than 120 °C [25]. Moreover, it is generally accepted that the practical implementation of PEMFCs would require the use of proton exchange membranes with high proton conductivity under anhydrous conditions and above 100 °C [4]. In the specific case of direct methanol fuel cells (DMFCs), Nafion presents very high methanol permeability. Finally, its price remains high enough so that the use of Nafion membranes in fuel cells can still be considered inefficient from an economic perspective [28]. In comparison, ILs display high stability and conductivity at high temperatures. Since many ILs remain liquid at room temperature, they need to be immobilized as liquid phase in membrane materials to form an ideally non-leaching and stable solid film that can be used as separator, ensuring continuous operation with a minimal amount of ionic liquid as active phase. The use of ionic liquid-based polymer membranes is among the approaches adopted to incorporate ILs into the separator in fuel cells. Polymer membranes based on ILs mainly comprise supported ionic liquids membranes (SILMs), polymer inclusion membranes (PILIMs), polymerized ionic liquid membranes (PyILMs) and other ionic liquid/polymer composite materials. Polymer SILMs, which consist of a liquid phase (ionic liquid) supported on a porous material by capillary forces, are favoured by high surface areas, low amount of solvent and high efficiency in comparison with other liquid membranes. However, their main limitation derives from the lack of long-term stability since the IL phase tends to leave the pores. Alternatively, PILIMs are formed by immobilizing the ionic liquid into a polymer matrix, showing improved mechanical and chemical properties compared to SILMs. Polymerized ionic liquid (PyILs) membranes are formed by polymerizing IL monomers, combining the unique properties of ionic liquids and the general features of polymers resulting in solid film structures. PyILMs can be mainly prepared by homopolymerization and copolymerization techniques. Other IL membrane types are IL-based polymer gel membranes and polymer/ionic liquid composite membranes including functionalized materials. Figure 1 summarizes the most important polymer membrane types based on ILs [18].

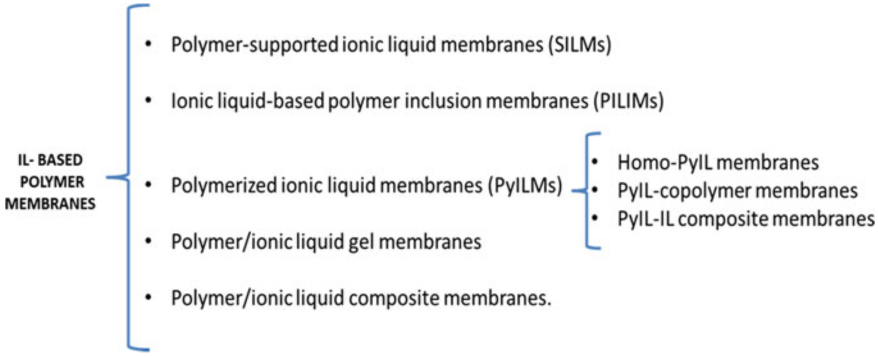


**Fig. 1** Classification of IL-based polymer membranes

Parameters such as thermal and chemical stability, compatibility of the polymer with the ionic liquid and polymer/ionic liquid ratio, are important factors that determine the final conductivity and the ionic liquid retention into the polymer matrix, and thus the overall performance of fuel cell devices.

The first attempts by Kreuer et al. [29] to create proton-conductive polymer membranes based on the imidazole molecule were made in 1998. Imidazole was employed as proton carrier in sulfonated poly(ether ether ketone) (SPEEK) membranes, showing high proton conductivity at high temperatures under anhydrous conditions. In 1999, Abu-Lebdeh and Owen [30] used room temperature eutectic mixtures of imidazole along with imidazolium salts in poly(vinylidene difluoride) (PVDF) membranes. The aim of such strategy was to create a network that served as proton transfer pathway by bonding a proton solvent (imidazole) to a polymer backbone. Later, Sun et al. [31] investigated polymer membrane systems based on Nafion and polytetrafluoroethylene (PTFE) impregnated with imidazole compounds. Since then, much progress has been made in order to create alternative polymer membranes based on ionic liquids. The following subsections will focus specifically on the application of ionic liquid-based polymer membranes in fuel cell technology.

## *4.1 Ionic Liquid/Polymer Membranes*

Polymer membranes allow ionic liquids to be prepared as solid electrolyte films for their application as separators in fuel cell devices. When ionic liquids are mixed with common polymers, which act as a plasticizer, their transport properties can be enhanced due to the increase of the ion dissociation and local dynamics in their structure [4]. Polymer membranes based on ILs can be relatively easily prepared by casting method, which consists of mixing the inert polymeric support with ionic liquid and an appropriate solvent such as tetrahydrofuran (THF). They can be also prepared by impregnating the polymer of interest with the ionic liquid in pure or solution form and by supporting the ILs onto porous polymer materials by other physical techniques such as ultrafiltration.

ILs including imidazolium cations have been the most commonly used to prepare IL polymer membranes for their application in proton exchange membrane fuel cells. In line with the work by Kreuer et al. [29], other authors have used sulfonated poly(ether ether ketone) as polymer matrix to prepare proton-conductive membranes due to its stability properties and low cost. 1-Ethyl-3-methylimidazolium diethyl phosphate has been combined with this type of polymers by casting method for their application in high-temperature PEMFCs under anhydrous conditions, with a resulting conductivity ranging between 1.25 and 3.16 mS cm$^{-1}$ (145 °C) and a maximum power density of 203 mW cm$^{-2}$ [32]. Another option is the impregnation of SPEEK membranes in aqueous solutions of ionic liquids. For example, SPEEK membranes impregnated with the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF$_4$], have proven to reach high conductivity values of up to 9.3 mS cm$^{-1}$ at 140 °C [33] with a maximum power density reported of 130 mW cm$^{-2}$ in PEMFCs at 80 °C [34]. In SPEEK membranes, the IL phase interacts with the sulfonic acid sites on the polymer through an ion exchange process. The conductivity of these membranes impregnated with the ionic liquid greatly improves with temperature when compared with the pure SPEEK membrane. However, membranes with a large amount of embedded ionic liquid can led to a decrease in conductivity due to an increase in the membrane resistance.

Several imidazolium-based IL membranes combined with poly(vinylidenefluoride-co-hexafluoropropylene) (PVdFHFP) have also been investigated. These include, among others, 2,3-dimethyl-1-octylimidazolium trifluoromethylsulfonate ([dmoim][TfO]), 1-butyl-3-methylimidazolium trifluoromethylsulfonate ([bmim][TfO]), *N*-ethylimidazolium trifluoromethyl-sulfonate ([eim][TfO]), 2,3-dimethyl-1-octylimidazolium bis(trifluoromethyl-sulfonyl)imide ([dmoim][TFSI]) and *N*-ethylimidazolium bis(trifluoromethanesulfonyl)imide ([eim][TFSI]) [35–38]. The resulting conductivity in such cases is within the interval 2–20 mS cm$^{-1}$. The power performance reported for these membranes in non-humidified fuel cells at inmerdiate and high temperatures are in the range 0.2–1.0 mW cm$^{-2}$. In these types of membranes, the thermal stability improves with higher amounts of polymer but there is a consequent decrease in the conductivity, and the polymer concentration needs to remain below 40 wt% so that the conductivity remains high (10$^{-2}$ S cm$^{-1}$ at room temperature).

Most of the imidazolium-based IL membranes reported in the literature have been prepared using monocationic ionic liquids. Dicationic ILs consisting of a double-charge cation formed by two individual cations bonded to each other through an alkyl chain and linked to respective anions of the same type are a new class of ionic liquids. Diatonic ILs can display superior properties compared to monocationic ILs in terms of thermal stability with conductivities of the order of those offered by monocationic ILs [39]. Cationic ionic liquids have been scarcely studied in membrane form in fuel cells. The performance of the dicationic IL 3-di (3-methylimidazolium) propane bis(trifluoromethylsulfonyl)imide, pr [mim]$_2$[Tf$_2$N], has been compared with that of the monocationic 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, [hmim][Tf$_2$N], in polybenzimidazole (PBI) membranes in high-temperature PEMFCs (180 °C). PBI is a non-shulphonated polymer with exceptional chemical and thermal stability. The conductivity of the membranes based on the dicationic IL is higher compared with the monocationic IL-based membrane, with a maximum power performance of 44 mW cm$^{-2}$ in the first case. Both membranes offer improved conductivity properties compared to standard phosphoric acid-loaded PBI membranes due to the inclusion of ionic liquid. The proton exchange in these composite membranes is mainly due to the Grotthus transport mechanism [40].

Several disadvantages have been reported for imidazolium-based polymer membranes. On one hand, imidazolium cations offer smaller electrochemical active surface areas compared with, for example, trimethyl amide and pyridinium groups. In addition, the performance of fuel cells based on ILs containing imidazolium cations can also be limited by the presence of impurities such as halide anions [41, 42].

IL liquids containing ammonium protic cations have recently gained more attention for the preparation of proton exchange membranes. The ionic liquid diethylmethylammonium trifluoromethanesulfonate, [dema][TfO], has been among the most studied PILs in fuel cells. Membranes based on this ionic liquid and sulfonated polyimide (SPI) prepared by casting method have been investigated in non-humidified $H_2/O_2$ fuel cells due to the high compatibility of both components. These membranes display thermal stability above 300 °C and an ionic conductivity higher than 10 mS $cm^{-1}$ (160 °C). The ratio of [dema][TfO] employed in SPI membranes can greatly affect the temperature dependence, being possible to achieve significant ionic conductivity at low temperature with high ratios of ionic liquid (>0.1 mS $cm^{-1}$ at 40 °C for a minimum ratio of 67 wt%). The high conductivity of such membranes has been linked to the strong interaction between the IL [dema][TfO] and the sulfonate groups of SPI. The maximum power densities reported at intermediate temperatures under non-humidified conditions range from 100 to 190 mW $cm^{-2}$ (at 80 and 120 °C, respectively) [43–45]. The same ionic liquid has been combined with PBI by casting method for their application in anhydrous $H_2/Cl_2$ fuel cells. These membranes showed an ionic conductivity of 20.7 mS $cm^{-1}$ at 160 °C, ensuring good chloride and hydrogen electrode kinetics. The maximum power density achieved so far in this type of fuel cell is 30 mW $cm^{-2}$ at 140 °C [46]. Other ILs with very similar structure to [dema][TfO] such as triethylammonium trifluoromethanesulphonate, [$N_{133}$][TfO], have been supported on high-porosity polyimide (Matrimid®), exhibiting conductivities in the same order (20 mS $cm^{-1}$ at 130 °C) [47]. The proton-conducting mechanism in this type of ionic liquids has been explained by both proton hopping (Grotthuss mechanism) and diffusion (vehicular mechanisms) [46, 48].

It is also possible to dope polymer membranes with ionic liquid cations or anions in order to improve some of their properties. Both imidazolium and ammonium ILs have been employed to dope Nafion materials to enhance their permeability, thermal stability and proton conductivity at high temperature, which are some of the limitations displayed by Nafion membranes as commented in previous sections. This technique has proven to offer good results when it comes to reducing the permeability of Nafion-based membranes in direct methanol fuel cells (DMFCs), which is a critical factor in this type of fuel cells. For example, the incorporation of the cation *n*-dodecyltrimethylammonium, [DTA], into the structure of a protonated Nafion-112 membrane can reduce the permeability of the membrane towards methanol by 80%. However, this strategy requires the determination of the optimal incorporation degree, since this modification in the polymer structure can lead to a significant increase in the membrane resistance. Optimal values of 20% could give the optimum membrane performance in such cases [49]. Polymer electrolyte membranes doped with PILs are also a promising material option for anhydrous proton conduction. Protic ionic liquids such as triethylammonium methanesulfonate and triethylammonium perfluorobutanesulfonate have been used for anion-doping in Nafion-117 membranes, increasing their high thermal stability up to 140 °C [50]. Other more complex approaches include sequential doping steps such as neutralizing Nafion 117 with e.g. triethylammonium, [TEA], and then doping it with the IL of interest, e.g. the protic ionic liquid triethylammonium trifluoromethanesulfonate, [dema][TfO]. By this technique, the resulting IL polymer membrane can increase its thermal stability up to 155 °C and its conductivity up to 7.3 versus 6.1 mS cm$^{-1}$ for Nafion-117 membrane at high temperature (145 °C) [51]. In such cases, hydrogen bonding interactions appear between the acidic sites (N–H) of the ammonium cations and the $SO_3^-$ groups in Nafion or in the trifluoromethanesulfonate anion. The distribution of these $SO_3^-$ groups around the ammonium cations increases with the concentration of ionic liquid. An increase in temperature and doping level leads to a faster diffusion capacity in the membrane structure and thus to a higher ionic conductivity [52]. Therefore, the IL uptake, the interaction between the ionic liquid and the polymer used and the structuration of the ionic liquid in the membrane matrix are of key importance in such strategies [53].

Other IL groups have shown great potential for their application in PEMFCs. This is the case of ILs containing fluorohydrogenate anions such as *N*-ethyl-*N*-methylpyrrolidinium fluoro-hydrogenate [EMPyr(FH)$_{1.7}$F]. PVdFHFP membranes based on this IL have displayed conductivities above 40 mS cm$^{-1}$ at 120 °C and a maximum power density of 103 mW cm$^{-2}$ at 50 °C under non-humidified conditions in PEMFCs [54].

The application of ionic liquids as exchange membranes has not restricted to intermediate- and high-temperature fuel cells. Very recently, IL-based polymer membranes have been investigated as separators in fuel cells operating at room temperature as is the case of microbial fuel cells (MFCs). Ionic liquids including imidazolium and ammonium cations supported on hydrophilic polyamide (Nylon) by ultrafiltration have been investigated as alternative separators in these devices. This includes ionic liquids based on the cations 1-*n*-alkyl-3-methylimidazolium (*n*-butyl, *n*-octyl) and methyl trioctylammonium, in combination with hexafluorophosphate, tetrafluoroborate, chloride and bis{(trifluoromethyl)sulfonyl}imide anions. Among these SILMs, the membrane based on methyltrioctylammonium chloride, [mtoa][Cl], showed the best performance in terms of power density and removal of organic matter from wastewater used as fuel in MFCs. However, the stability of this type of IL-based membranes is limited in contact with aqueous media as happens in MFCs [55]. Instead, ionic liquid polymer inclusion membranes prepared by casting method have received more attention in microbial fuel cells (Fig. 2). Membranes of polyvinyl chloride (PVC) and ionic liquids with imidazolium, ammonium and phosphonium cations have shown potential application in such devices [56, 57]. Although imidazolium and ammonium-based ILs have been among the most studied types, several ILs containing phosphonium cations offer good conductivity and their combination with an aromatic anion improves the movement of ionic charges. For example, the IL triisobutyl(methyl)phosphonium tosylate, [$P_{I4,I4,I4,1}$][TOS], contains a sulfonil group, also present in Nafion, that may act as a proton-conductive group. Phosphonium-based IL polymer membranes have been compared with Nafion in single-chamber MFCs, offering equivalent power densities (794 vs. 755 mW m$^{-3}$, respectively). The stability of PILIMs in aqueous media is one of the key factors for the long-term operation in microbial fuel cells [58]. In this respect,

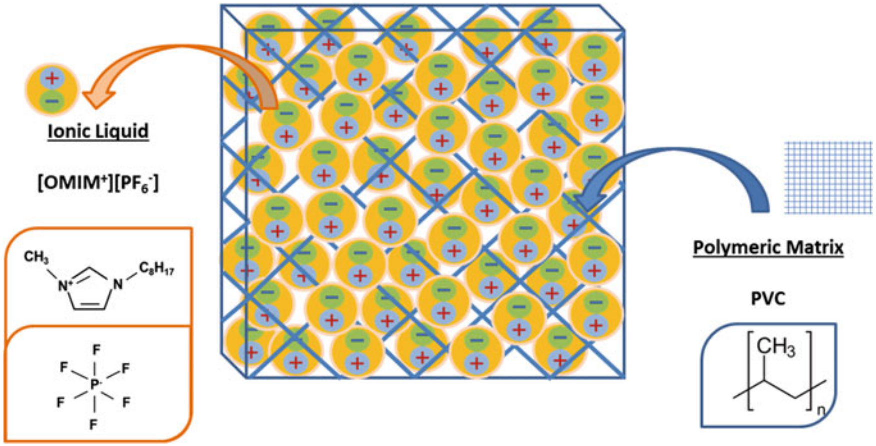


**Fig. 2** IL polymer inclusion membranes used in MFCs

ionic liquids containing anions susceptible to hydrolysis can severely affect fuel performance, as occurs with the anion hexafluorophosphate [$PF_6^-$] [57].

Another advantage of PILIMs is that they can be embedded in several types of conducting materials for fuel cell construction and upscaling. PILIMs can be embedded into cathode materials such as carbon cloth to create cathode–membrane assemblies, reducing the electrode spacing. This option can significantly improve fuel cell performance compared with setting up a PILIM and a carbon-based cathode as separate components (e.g. methyltrioctylammonium chloride) [59]. This configuration based on the ionic liquid triisobutyl(methyl)phosphonium tosylate, [$P_{I4,I4,I4,1}$][TOS], has been employed in upscaled continuous mode MFCs, achieving notable level of power density (12.3 W $m^{-3}$) and high percentage of chemical oxygen demand (COD) removal when using wastewater as fuel [16]. As MFCs use several types of wastes of different nature as fuel, the possible interaction between the ionic liquid used as electrolyte and the composition of the medium need to be carefully studied in order to ensure an optimal performance.

## *4.2 Polymerized Ionic Liquid Membranes*

The innovative idea of applying polymerized ionic liquids in fuel cell technology is quite young and has opened up a promising path for fuel cell membrane development. Poly(ionic liquid)s (PyILs) or polymerized ionic liquids are polyelectrolytes whose structure is made of repeating units based on ionic liquids. Although ILs are often liquid at room temperature, the complex macromolecular structure of

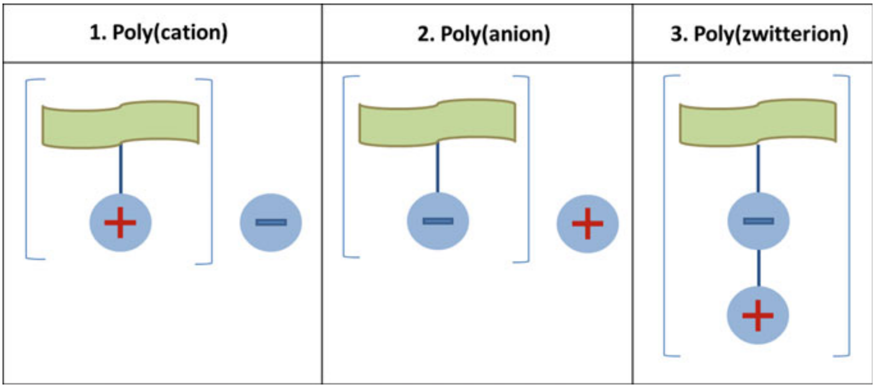


**Fig. 3** Most common monomer units of polymerized ionic liquids [4]

PyILs makes most of them solid [60, 61]. PyILs are usually synthetized by direct radical polymerization of ILs. They can be grouped in polycations bearing a cation, polyanions bearing an anion and polyzwitterions (bearing a cation and an anion), although other structures are possible [62] (see Fig. 3).

Polymerized ionic liquids can be prepared by two different techniques: (i) direct polymerization of ionic liquid monomers, and (ii) chemical modification of polymers. While ILs are characterized by high conductivity (up to 10 mS $cm^{-1}$), Polymerized ionic liquids by these techniques exhibit ionic conductivities below $10^{-3}$ mS $cm^{-1}$ since the glass transition temperature increases after the polymerization process, with a lower number of mobile ions available. However, several methods have been developed to enhance the ionic conductivity of PyILs such as: (i) using a higher concentration of the carrier ions and (ii) modifying the structure of the electrolyte [4]. Their solid state reduces the possibility of leakage in fuel cells compared with non-polymerized ionic liquids. PyILs have also been used as dispersant to stabilize different types of materials. Finally, their porous structure makes them useful for many commercial applications such as ion exchange materials, metal recovery or liquid chromatography [60].

The ionic conductivity of PyILs makes them suitable for preparing different types of exchange membranes. A wide variety of Polymerized ionic liquid-based membranes can be synthesized depending on their specific applications. Díaz et al. [63] performed the polymerization of 1-(4-sulfobutyl)-3-vinylimidazolium trifluoromethanesulfonate ([$HSO_3$-bvim][TfO]) to obtain a solid electrolyte membrane. The imidazolium cation was selected due to its high electrochemical stability while the triflate anion was chosen because of its high conductivity. This material was used as separator in proton exchange membrane fuel cells (PEMFCs), with a maximum power output of 33 mW $cm^{-2}$ at room temperature. They also observed that the thickness of the membranes plays an important role in terms of proton transfer resistance. Later, Díaz et al. [64] photopolymerized 1-(4-sulphobutyl)-3-vinylimidazolium trifluoromethanesulphonate, [$HSO_3$-bvim][TfO], and the ionic liquid 1-(4-sulphobutyl)-3-methylimidazolium trifluoromethanesulphonate, [$HSO_3$-bmim][TfO], for achieving values of conductivity of 290 S $cm^{-1}$ and a maximum power density of 49 mW $cm^{-2}$ operating at 40 °C. All these works show how quick the field of polymerized ionic liquids is being developed and their high potential as separators in fuel cells. Thus, the replacement of commercial membranes such as Nafion could take place in the near future.

These ionic liquid-based polyelectrolytes have also been used to prepare anion exchange membranes for alkaline fuel cells (Fig. 4). Lin et al. [65] crosslinked 1-vinyl-3-methylimidazolium iodide ([vmim][I]) with styrene and acrylonitrile to obtain an anion exchange membrane with hydroxide ions in its structure. The hydroxide ion conductivity was higher than 10 mS $cm^{-1}$ and good mechanical and chemical properties were obtained in alkaline conditions at 60 °C. Qiu et al. [66] also crosslinked styrene and acrylonitrile with 1-allyl-3-(6-(1-butyl-2-methylimidazol-3-ium-3-yl)hexyl)-2-methylimidazol-3-ium bromide ([abmhm][$Br]_2$), to fabricate AEMs. This material showed a hydroxide conductivity of approximately 20 mS $cm^{-1}$ and long-term stability in alkaline solutions even at temperatures above 50 °C. Qiu et al. [67] also compared the performance of two types of copolymer membranes based on ionic liquids as AEMs. Membranes based on 1-methyl-3-(4-vinylbenzyl)imidazolium chloride ([mvbim][Cl]), and *N*,*N*,*N*-trimethyl-1-(4-vinylphenyl) methanaminium chloride ([tmvpma][Cl]), exhibited

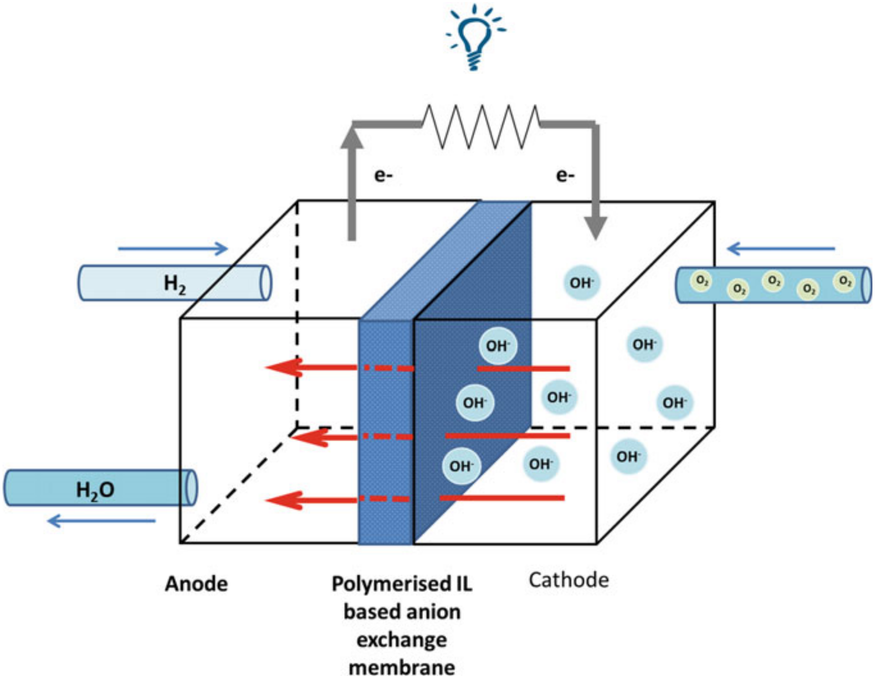


**Fig. 4** Scheme of a double chamber alkaline fuel cell using a polyionic liquid separator

hydroxide conductivities up to 10 mS $cm^{-2}$. In general, imidazolium-based ILs have shown better chemical stability under alkaline conditions versus ammonium ILs, since membranes based on quaternary ammonium salts can be subjected to degradation processes in alkaline solutions.

Finally, there are several research works reporting promising results on the use of PyILs in quasi-solid state dye-sensitized solar cells (DSSCs). The application of ILs in DSSCs has increased their efficiency. For instance, the use of imidazolinium cations in DSSCs leads to the decrease of recombination at the working electrode due to the multilayer adsorption, thus improving the DSSC performance [68]. The long-term stability of DSSCs has also been enhanced by replacing liquid electrolytes by solid state PyILs electrolytes [69–72].

## 4.3 IL Gel and Composite Polymer Membranes

This subsection includes other strategies to prepare polymer membranes based on ionic liquids such as gel polymer membranes, polymerization techniques and other IL-based polymer membrane composites that also contain non-polymer functionalized materials.

The sol–gel transition of polymers in ILs is another option to simply fabricate polymer electrolyte membranes. Imidazolium-based ILs such as 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([$C_2$mim][TfO]) can be used with poly [(vinylidene fluoride)-co-hexafluoropropylene] P(VdF-co-HFP), to form polymer gels with still high ionic conductivity. The resulting gel membrane has a porous structure which has been associated with the presence of spherulites formed during the sol–gel transition of the polymer in the IL [26]. Also, vinyl monomers such as methyl methacrylate can be easily polymerized by free radical polymerization when solubilized in ILs. The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluromethanesulphone) imide ([$C_2$mim][$Tf_2N$]) has been employed to fabricate polymers gel of high ionic conductivity in the order of 10 mS $cm^{-1}$ using this technique [4]. These gel membranes showed high potential for their applications in fuel cells.

The polymerization of ionic liquid microemulsions, which are stable dispersions containing two immiscible liquid phases stabilized by surfactants, has proven to be a suitable technique for the preparation of IL gel polymer electrolyte membranes. IL-based microemulsions are gaining growing interest due to the outstanding properties of both the microemulsion system and the ionic liquid. Several examples of protic ionic liquid microemulsions can be found in the literature. Yan et al. [73] fabricated proton-conducting membranes via polymerization of microemulsions of PILs dispersed in polymerizable oil (mixture of styrene and acrylonitrile). The resulting membranes based on the PILs *N*-methylimidazolium trifluoromethanesulfonate ([mim][TfO]), *N*-ethylimidazolium trifluoromethanesulfonate ([eim][TfO]) and 1,2-dimethylimidazole trifluoromethanesulfonate ([dmim][TfO]), showed similar proton conductivities up to 100 mS $cm^{-1}$ at 160 °C.

Polymerized IL microemulsions pose, however, several challenges such as their long-term stability, since the ionic liquid contained in the membrane structure can be released to the media. In line with this work, Chu et al. [74] fabricated proton-conducting membranes based on polyamidoamine dendrimers based on PILs. Polyamidoamine dendrimers are monodisperse polymers characterized by high concentration of primary and tertiary amine groups. This type of dendrimers can be easily protonated to form macromolecular cationic centres of PILs via neutralization with Brønsted acids. The membrane composites can be fabricated by cross-linking polymerizable oils containing this polyamidoamine dendrimer type, showing very high thermal stability (up to 350 °C) and proton conductivity of the order of 12 mS $cm^{-1}$ at 160 °C. Membranes based on this type of macromolecular PILs display higher conductivity compared with the same type of membranes containing small molecule PILs. Other alternative materials for proton-conducting membranes include silica hybrid separators based on PILs. Lin et al. [75] prepared PIL-based hybrid membranes by polymerizing a mixture of 1-ethylimidazolium trifluoromethane-sulfonate ([eimm][TfO]), and a polymer precursor, poly (styrene-co-acrylonitrile), in which silica fillers were dispersed (silica nanoparticles and mesoporous silica nanospheres). Under anhydrous conditions, these hybrid membranes exhibit proton conductivities up to 10 mS $cm^{-1}$ at 160 °C. However, the power performance of these membranes in fuel cells has not been thoroughly investigated yet.

As commented above, polybenzimidazole has been extensively investigated doped with several inorganic acids for high temperature applications up to 200 °C. Recently, PBI membranes based on different inorganic fillers and ionic liquids have been fabricated in order to improve crossover properties of PBI membranes at high temperatures. PBI gel electrolytes can be synthesized containing acid along with ionic liquid and polymer material as potential proton exchange membranes for high-temperature PEMFCs. For example, composites consisting of the acid $H_3PO_4$, the ionic liquid 1-methyl-3-propyl-methylimidazolium dihydrogen phosphate and PBI display ionic conductivities in the order of 2 mS $cm^{-1}$ (150 °C) under anhydrous conditions. These membrane composites show high thermal stability (up to 200 °C). A three-dimensional hydrogen bonding network has been proposed for this type of composite, with predominance of the Grotthuss hopping mechanism [76].

Another recent approach consists of the development of polymer composites based on ion exchange materials functionalized with ionic liquid in order to improve their proton conductivity. Xu et al. [77] developed a composite membrane formed by poly(benzimidazole) loaded with $H_3PO_4$ and graphite oxide doped with the ionic liquid 1-(3-aminopropyl)-3-methylimidazolium bromide, [apmim][Br]. The inclusion of graphite oxide functionalized with the cation group 1-(3-aminopropyl)-3-methylimidazolium allows the proton conductivity to be improved from 25 to 35 mS $cm^{-1}$. The performance of this type of membranes in PEMFCs can reach 320 mW at 175 °C. The improvement of proton conductivity in comparison with PBI membranes solely loaded with $H_3PO_4$ can be explained by the presence of hydrogen bonds in the IL functionalized graphite, forming acidic functional groups, such as carboxylic acid, epoxy oxygen and especially the aminopropyl-methyl imidazolium group, which facilities proton conduction.

Finally, hybrid IL polymer membranes have been prepared by adding large pore zeolites functionalized with protic ionic liquids in $H_2PO_4$-doped PBI membranes via casting solution (Fig. 5). $NH_4$-BETA and NaY zeolite types have a porous structure that allows accommodating a wide variety of cations. They have been functionalized with imidazolium and ammonium-based ionic liquids such as trimethylammoniun dimethyl phosphate, *N*,*N*-dimethyl-*N*-(2-hydroxyethyl)ammonium bis(trifluoromethanesulfonyl)imide and 1-H-3-methylimidazolium bis (trifluoromethanesulfonyl)imide to fabricate proton exchange composite membranes. The IL/zeolite/PBI composites offer satisfactory performance for long-term operation with sufficient conductivity (32 mS $cm^{-1}$ at 150 °C). The inclusion of this type of filler in the PBI membrane leads to a decrease in the fuel crossover due to molecular sieving properties of the inorganic loading and the improved organic–inorganic interface owing to the presence of new functional groups. Moreover, the promotion of the ionic conductivity is the result of a higher phosphoric acid uptake and the presence of new conduction pathways [78].

All these advances show the great possibilities of ionic liquids in the field of fuel cell polymer membranes. Given that the use of these compounds in fuel cell

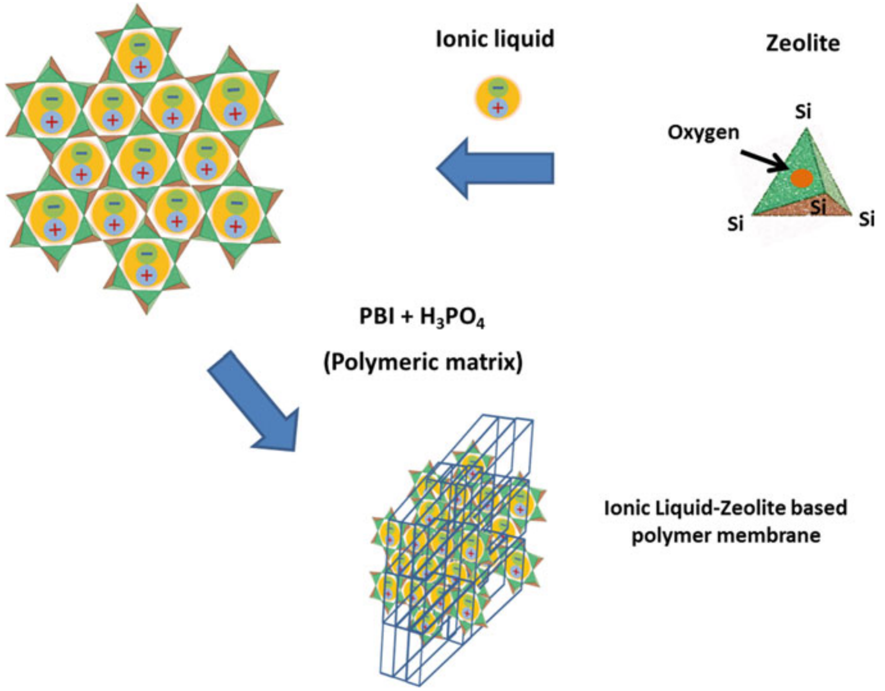


**Fig. 5** Ionic liquid–zeolites polymer membranes

technology is fairly recent, much progress on the development of IL polymer membranes for fuel cell applications is expected to be made in next years.

## 5 Conclusions

The main advantages of using ionic liquids as fuel cell electrolytes are their liquid near-zero vapour pressure, thermal and chemical stability, task-specific properties and high ion and proton conductivities. Polymer membranes based on ILs are a promising alternative to perfluorosulphonic acid membranes such as Nafion, which is one of the most used electrolytes in fuel cells but pose operational and cost limitations. In comparison, IL-based polymer membranes can display high conductivity and stability at high temperature under non-anhydrous conditions. Several techniques have been developed to fabricate IL-based polymer membranes, including supported membranes, impregnated membranes, polymer inclusion membranes by casting method and, more recently, the polymerization of ionic liquids as one of the most innovative techniques. Other types are IL gel and hybrid IL polymer composite materials. The compatibility between the polymer and the ionic liquid used as well as the ionic liquid/polymer ratio are key factors for ensuring a good conductivity and mechanical stability. IL polymer membranes have been successfully investigated mainly in proton exchange membrane fuel cells, but also in other types of fuel cells such as alkaline and microbial fuel cells, which operate at room temperature. All these facts make ionic liquids ideal candidates for fuel cell separators and thus for promoting fuel cell technology.

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