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PROGRESS IN THE USE OF IONIC LIQUIDS AS ELECTROLYTE MEMBRANES IN FUEL CELLS

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ABSTRACT

This work provides a critical review of the progress in the use of Room Temperature Ionic Liquids (RTILs) as Proton Exchange Membrane (PEM) electrolytes in Fuel Cells (FCs). It is well-known that for an efficient early commercialisation of this technology it is necessary to develop a proton exchange membrane with high proton conductivity without water dependency capable of working at temperatures above 100 ºC. The use of ionic liquids as electrolytes in electrochemical devices is an emerging field due to their high conductivity, as well as their thermal, chemical and electrochemical stability under anhydrous conditions. This paper attempts to give a general overview of the state-of-the-art, identifies the key factors for future research and summarises the recent progress in the use of ionic liquids as an innovative type of PEMs.

1. INTRODUCTION

The need to reduce our dependence on fossil fuels and the generation of pollutants has led to the development of proton exchange membrane fuel cells (PEMFCs) as promising alternatives for clean power generation, particularly due to their high efficiency and low emissions. This technology facilitates the adequate performance and durability needed to compete with conventional technologies and it will likely be commercialised in the medium term for transportation and portable applications. The number of publications (figure 1) describing fuel cells in the last decade shows the increasing interest in this technology.

Fuel cells are electrochemical devices able to convert chemical energy directly into electrical energy. They can be classified based on their operating temperature and

electrolyte: alkaline fuel cells (AFCs), proton exchange membrane fuel cells (PEMFCs), phosphoric acid fuel cells (PAFCs), molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs). PEMFCs, which can be fed with hydrogen or methanol (Direct Methanol Fuel Cells, DMFCs), are generally used for portable applications and transportation because they hold several advantages over conventional technologies, such as their high electrical efficiency, silence, low pollutant emissions, ease of installation and rapid start-up.

A PEMFC is composed of different fundamental elements: bipolar plates, diffusion layers, electrodes (anode and cathode) and the electrolyte. A schematic of a PEMFC is shown in figure 2. The core of a PEMFC is called the membrane electrode assembly (MEA), and it is composed of the proton exchange membrane (PEM) placed between two electrodes. Proton exchange membranes have different functions, such as separating the gaseous reactants, conducting protons from the anode to the cathode, electrically insulating the electrons and supporting the catalyst [1]. Membranes should meet the following requirements to be applied in PEMFCs [2]:

- High proton conductivity in both dry and wet states
- Outstanding mechanical strength and dimensional stability
- Chemical, electrochemical and thermal stability under the operating conditions
- Low fuel and oxygen crossover
- Easy conformation to form a membrane electrode assembly
- Competitive cost

Perfluorosulfonic acid ionomer, being Nafion the most representative ionomer of this category (figure 3), is the most widely used membrane in PEMFC devices because of its excellent chemical stability, high ionic conductivity and good mechanical strength [3, 4]. However, the conductivity of Nafion drops at temperatures above 100 ºC due to the evaporation of water which is critical for proton conduction. Higher temperatures are desirable because tolerance of the catalyst to contaminants is improved and hydrogen with less purity can be used. Moreover, an increase in temperature enhances the electrode reaction rates [5]. Table 1 compares the five different types of membranes frequently used in PEMFCs [1, 2].

Table 1. General overview of different PEMs

	Structure	Advantages	Disadvantages
Perfluorinated membranes	-Fluorinated backbone -Fluorocarbon side chain -Ionic clusters consisting of sulphonic acid ions attached to side chains	-Excellent chemical and electrochemical stability -High proton conductivity	-Expensive -High methanol crossover -Dehydration above 80 ºC
Partially fluorinated membranes	-Fluorocarbon base -Hydrocarbon or aromatic side chain grafted onto the backbone	-Inexpensive commercial base films -Low crossover -Base matrix with good anti-free radical oxidation -Relatively strong compared to perfluorinated membranes	-Less durable -Low performance
Non-fluorinated membranes	-Hydrocarbon or aromatic base, typically modified with polar or sulphonic groups	-Low cost -Low crossover -Proton conductivity comparable to Nafion at a high water uptake	-High swelling -Inadequate durability
Acid-base membranes	-Incorporation of acid component into an alkaline polymer base	-High thermal, dimensional and chemical stability -Proton conductivity comparable to Nafion	-Durability
Ionic liquid membranes	-Formed from an organic cation and an organic/inorganic anion	-Tunable -High conductivity -High chemical, electrochemical and thermal stability -Non-volatile	-Difficulty constructing a solid membrane

During the last few years, significant progress in cost, durability and performance of fuel cells has been made, but the remaining technical and economic issues must be solved before this technology can be commercialised. Several authors have focused on the optimization of the stack design and the fuel cell configuration. Other aspects that require improvement include the structure and composition of the catalyst layer. For the electrolyte, many efforts have been made to develop a PEM with high conductivity at low relative humidity to reduce the cost and complexity of the system. Besides, the development of non-volatile and non-flammable electrolytes is important in order to improve the safety and durability of fuel cells. Consequently, several studies have incorporated ionic liquids as electrolytes in PEMFCs under anhydrous conditions [6, 8]. Ionic liquids have been expected to overcome the problems of volatile electrolytes while they are characterised by excellent ionic conductivities even under anhydrous conditions.

This review will summarise the recent progress in the PEM field with special attention to those systems that incorporate ionic liquids and identify the key factors for future

research. First, a short review of conventional electrolytes is reported highlighting the achievements and future challenges for implementation of FCs at larger scale.

2. CONVENTIONAL PROTON EXCHANGE MEMBRANES

Perfluorosulphonic acid ionomer membranes (PFSI) are the most commonly used membranes in PEMFCs due to their excellent chemical and electrochemical stabilities, as well as their high proton conductivity. However, at high temperature the membrane dehydrates and its proton conductivity is highly reduced. Several efforts have been made to improve the performance of Nafion membranes and ensure water retention at high temperatures. One strategy for improving their performance is blending with organic or inorganic compounds [5]. However, the direct blending method generally decreases the proton conduction.

To overcome the drawbacks of perfluorinated membranes, alternatives such as the use of partially fluorinated membranes are being studied by many authors [9-17]. This technique allows the design of new better performing materials, improving their mechanical and thermal properties relative to the individual polymers. Besides, the cost of these membranes is reduced because a smaller amount of fluorinated polymer is required by means of the utilization of less expensive polymers. However, the proton conductivity can be compromised.

Non-fluorinated membranes might be alternative membranes for PEMFCs able to replace the expensive fluorinated membranes that have a high fuel crossover and limited operating temperatures. However, as similar to fluorinated acid membranes, these polymers require a proton conductor for use in fuel cell devices. Poly(arylene ether) materials are studied by many researchers because of their availability, processability, varied chemical compositions and high stability in the fuel cell environment [18-31]. However, poly(arylene ether) membranes present short lifetime and excessive swelling. Other encouraging non-fluorinated materials as PEMs are sulphonated polyimides (SPIs) because of their excellent mechanical and thermal properties, as well as their chemical stability and low crossover [32-36].

Another promising alternative developed by many authors consists of blending basic polymers with strong acids. These membrane electrolytes have high proton conductivities even under non-humidified conditions. The basicity of these polymers permits the formation of hydrogen bonds with the acid. H_3PO_4 and H_2SO_4 show effective proton conductivity, even in their anhydrous form, due to their exceptional proton conduction mechanism; this mechanism utilises self-ionisation and self-dehydration [37, 38]. Among the basic polymers, polybenzoimidazole (PBI) (figure 4) has received significant attention due to its excellent thermal and chemical stability [39-51]. However, high acid content results in high conductivities, but the mechanical stability is reduced. Moreover, the loss of the acid component during operation limits the application of these membranes.

Conventional proton exchange membranes have been widely investigated by many researchers as electrolytes for fuel cell applications. However, it is indubitable that these membranes require improvements in order to achieve a real implementation of

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this technology. Several works are related to the modification of Nafion membranes towards improving their water retention and proton conduction at high temperatures. For this purpose, several authors have studied bifunctional compounds incorporated in a Nafion matrix. These bifunctional compounds include functionalised silica, multi-walled carbon nanotubes (MWCNTs) and zeolites [52-58]. The use of non-fluorinated polymers, as a total or partial replacement of fluorinated polymers, is a less expensive alternative for PEM applications. However, as in the case of fluorinated membranes, they require a proton conductor. PBI/H_3PO_4 blends are a feasible alternative for PEMFCs. Nevertheless, issues related to the mechanical stability and durability must be addressed. It is still necessary the development of a proton exchange membrane which satisfies all the requirements namely, proton conductivity high enough at high temperature, durability, mechanical and chemical stability and a reasonable cost for the implementation of the fuel cell technology.

## 3. IONIC LIQUIDS FOR FUEL CELL APPLICATIONS

Ionic liquids are organic salts with melting points below or equal to room temperature. They have attractive properties, such as negligible volatility, non-flammability, high thermal and electrochemical stability and outstanding ionic conductivity even under anhydrous conditions. They are formed entirely by ions and differ from ionic solutions in that ionic liquids do not contain a solvent (figure 5). Some ions that are frequently used in ionic liquids are shown in figure 6. Because ionic liquids are formed entirely of ions, they can be combined to meet the desired properties for specific applications [59]. In particular, the use of ionic liquids in electrochemical devices such as dye-sensitised solar cells, supercapacitors, lithium batteries, actuators and fuel cells has been studied extensively [60, 61].

The conductivities of ionic liquids at room temperature range from 1.0×10^{-4} - 1.8×10^{-2} S cm^{-1}. Generally, conductivities of approximately 1.0×10^{-2} S cm^{-1} are typical of ionic liquids based on dialkyl-substituted imidazolium cations. Ionic liquids based on tetraalkylammonium, pyrrolidinium, piperidinium and pyridinium cations have lower conductivities, ranging from 1.0×10^{-4} to 5×10^{-3} S cm^{-1}. The reduction potential of a cation and that of anion oxidation depends on the counter-ion. Therefore, halide anions, such as F$^-$ and Br$^-$, limit the stability to 2-3 V. However, bis(trifluoromethylsulphonyl)imide anions (Tf$_2$N$^-$, is also found in the literature as TFSI) is oxidised at a high anodic potential, allowing stabilities approximately 4.5 V [62]. Ionic liquids based on tetraalkylammonium cations showing cathodic reduction at moderately negative potentials are characterised by an enhanced stability of approximately 4.0-5.7 V [63].

Two general types of ionic liquids exist: aprotic and protic. Aprotic ILs are characterised by a low melting point related to the difficulty of packing large irregular cations with small anions. These materials have a high mobility and ion concentration, making them suitable electrolytes for lithium batteries. Protic ionic liquids have a mobile proton located on the cation. The reactivity of this active proton makes them appropriate for use as electrolytes in fuel cell applications [64].

3.1. IONIC LIQUIDS AS ELECTROLYTES IN PEMFCs

Protic ionic liquids can be easily obtained by combining a Brønsted acid and a Brønsted base. These materials can transfer protons from the acid to the base, leading to the presence of proton donor and acceptor sites that can be used to build a hydrogen-bonded network [65]. Moreover, in most protic ionic liquids, the proton migration occurs through a vehicular mechanism: protic ionic liquids with the highest conductivities are those with highest fluidities [66]. A benefit of using protic ionic liquids is that cells can be operated at temperatures above 100 ºC under anhydrous conditions because the proton transport is independent of the water content. The synthesis of protic ionic liquids is based on an acid-base neutralisation reaction: a proton is transferred from a Brønsted acid to a Brønsted base:

$$HA + B \rightleftarrows BH^+ + A^-$$
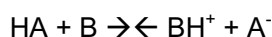
This proton transfer is a widely used technique for the synthesis of ionic liquid, but the issue of vapor pressures requires a greater deepening. The large decrease of the partial pressures characteristic of the pure acid and pure base due to the free energy decrease associated with proton transfer is responsible for the low vapor pressures. When the free energy change in the proton transfer process is large, the proton may become localized on the Brönsted base and the probably of reforming an acid molecules (HA) becomes negligible at room temperatures. Due to the strong coulomb interaction between ions and the long range of the interaction, the vapor pressure over the liquid is very low. The properties of protic ionic liquids are influenced by their degree of ionization. The classical Walden rule is used as a way of assessing the ionicity of ionic liquids [67, 68].

Different research groups have studied protic ionic liquids in PEMFCs. Nakamoto and co-workers prepared a protic ionic liquid and ionic melts combining bis(trifluoromethanesulphonyl)imide and benzimidazole (BIm) at various molar ratios. The protic neutral salt formed by a mixture at the equivalent molar ratio had a thermal stability above 350 ºC while remaining hydrophobic and stable during electrode reactions (H_2 oxidation and O_2 reduction). A proton conductivity of 8.3 x 10^{-3} S cm^{-1} was achieved at 140 ºC. The electrochemical polarisation was evaluated using cyclic voltammetry at 150 ºC under non-humid conditions. Operation under non-humid conditions at 150 °C is possible when using the BIm-Tf_2N melts as electrolytes. Open circuit voltages are lower compared to a fuel cell using H_3PO_4 as the electrolyte under the same conditions, although higher current densities are available at low operating voltages for the BIm-Tf_2N cells [69]. In a study conducted by Noda et al. [70] Brønsted acid-base ionic liquids were prepared by mixing different molar ratios of solid imidazole (Im) and solid bis(trifluoromethanesulphonyl)imide. The mixture with an equivalent molar ratio formed a protic neutral salt that was thermally stable above 300 ºC. The Im molecule not only functions as a proton carrier but also improves the O_2 reduction and H_2 oxidation reactions, acting as a H^+ donor and acceptor respectively. Through cyclic voltammograms, fuel cell tests under non-humidifying conditions were performed, showing that at prolonged potential cycling, the electric current decreased gradually. This behaviour was possibly attributed to the adsorption of Im onto the electrode surface. Yoshizawa-Fujita et al. [71] reported the use of 3-(1-butyl-1H-imidazol-3-ium-

3-yl)propane-1-sulphonate mixed with three different acids (HTf$_2$N,CH$_3$SO$_3$H and CF$_3$SO$_3$H) as proton transport electrolytes. The ionic conductivity of the HTf$_2$N mixtures increased with the HTf$_2$N content up to 50 mol%. Beyond that ratio, the ionic conductivity no longer increased (1.0 x 10^{-3} S cm^{-1} at 100 ºC). For CH$_3$SO$_3$H and CF$_3$SO$_3$H, the maximum conductivity was obtained at a 90 mol% acid content for both compounds (1.0 x 10^{-2} S cm^{-1} at 100 ºC). The glass transition temperature (Tg) of mixtures containing CH$_3$SO$_3$H or CF$_3$SO$_3$H decreased linearly when increasing the acid content, while the Tg of HTf$_2$N mixtures decreased when increasing the acid content up to 50 mol% before stabilising near -55 °C.

Ionic liquids can be mixed with organic or inorganic compounds to improve their physical and chemical properties [72-75]. Accordingly, inorganic glasses have excellent thermal and chemical stability, high mechanical strength and low cost. Hybrid proton exchange membranes based on diethylmethylammonium trifluoromethanesulphonate ([dema][TfO]) and SiO$_2$ monoliths were developed by Li et al. [76]. These membranes exhibited very high anhydrous ionic conductivities, exceeding 1.0 x 10^{-2} S cm^{-1} at 120-220 ºC. Nevertheless, the brittleness of the membrane must be improved for future applications in fuel cells. Clays are widely used due to their abundance, availability, high sorption and low cost. They usually exist as layered structures and may be used as host materials when fabricating hybrid composites. In a study carried out by Takahashi and co-workers [77] three different ionic liquids were intercalated into montmorillonite clay, 1-ethyl-3-methylimidazolium octylsulphate ([EMI][OcSO$_4$]), N,N,N-trimethyl-N-propylammonium bis(trifluoromethanesulphonyl) imide ([TMPA][Tf$_2$N]) and N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis (trifluoromethanesulphonyl) imide ([DEMET][Tf$_2$N]). Ionic conductivities of 1.99 x 10^{-3} S cm^{-1} and 1.88 x 10^{-3} S cm^{-1} were achieved for [TMPA][Tf$_2$N]/montmorillonite and [DEMET][Tf$_2$N]/montmorillonite, respectively. The thermogravimetric and differential thermal analyses (TG-DTA) of the three types of intercalated MILs showed an improved thermal stability compared to ILs.

Luo and Zhao [78] synthesised non-glass inorganic-organic hybrid membranes from tetraethoxysilane (TEOS), 3-glycidyloxypropyltrimethoxysilane (GPTMS), trimethyl phosphate (PO(OCH$_3$)$_3$) and diethylethylammonium trifluromethanesulphonate. PO(OCH$_3$)$_3$ was usually added to improve proton conductivity. The hybrid membrane was fabricated by the sol-gel process, and the average thickness of the hybrid membranes was approximately 1 mm. The quantity of the different silicon sources influenced the membrane tenacity, showing that increasing the TEOS content hardens the membrane. The Tg curves with different amounts of [dema][TfO] showed a weight loss of 2% from 30 ºC to 120 ºC that was attributed to the loss of water in the Si-O-Si network. A second weight loss (approximately 4%) occurred at 160 ºC-240 ºC due to the decomposition of (RO)$_3$PO. When the temperature increased from 280 ºC to 500 ºC, a weight loss attributed to the decomposition of the side chains of the silicon source and the burning of organic [dema][TfO] was observed. The conductivity of the pristine membrane from 20 ºC to 220 ºC ranged from 1.0 x 10^{-7} to 1.0 x 10^{-6} S cm^{-1}. The conductivity increased with the ionic liquid content. Membranes containing 50 wt% ionic liquid had conductivity of 1.0 x 10^{-3} S cm^{-1} at 30 ºC and of 1.0 x 10^{-2} S cm^{-1} at 220 ºC.

While a great attention has been given to ammonium protic ionic liquids, phosphonium protic ionic liquids have deserved less attention as electrolytes despite the reported superior characteristics in terms of thermal and electrochemical stability, viscosity and

ionic conductivity. The work developed by Luo and co-worker [79] compares the physicochemical properties of phosphonium and ammonium protic ionic liquid with trioctyl and triphenyl groups. It was found that phosphonium based protic ionic liquids exhibit higher thermal stability that the corresponding ammonium based protic ionic liquids. In addition, the ionic liquids with octyl group report higher thermal stability in both phosphonium and ammonium ionic liquids. Phosphonium ionic liquids exhibited higher conductivity than their ammonium analogues, probably due to their weaker hydrogen bond and Coulombic interactions as well as higher carrier ion concentrations.

Ionic liquids are a viable alternative as proton conductors for PEMs. It has been well demonstrated that they provide high conductivities at high temperatures even in absence of water. However, the application of ionic liquid in fuel cell is in the early stage and further studies about the performance of these compounds in fuel cell environment are still required.

3.2. POLYMER-IONIC LIQUID MEMBRANES

Solidified electrolytes are preferable when employing ionic liquids as electrolytes because most electronic devices require film-like electrolyte materials. One approach towards achieving this quality is mixing an ordinary polymer with ionic liquids. This technique results in an improvement of the transport properties of the polymer electrolytes because the degree of ion dissociation, concentration of ionic moieties and Tg of the membrane are modified. The mixture can be prepared by polymerising various monomers in the presence of ionic liquids or by generating a simple mixture of polymers with ionic liquids [80]. However, this technique often results in compromises between the desirable RTIL properties and the mechanical strength of the membranes [75, 81].

Common vinyl monomers are soluble in common ILs and can be polymerised via free radical polymerisation. Therefore, the polymerisation of methylmethacrylate in 1-ethyl-3-methyl imidazolium bis(trifluromethanesulphone)imide ([C$_2$mim][Tf$_2$N]) with a small amount of a cross-linker generates self-standing, flexible and transparent polymer gels that can be obtained in a wide [C$_2$mim][Tf$_2$N] compositional range between 1/9 and 7/3. The ionic conductivity of the membranes with a high IL composition is approximately 1.0 x 10^{-2} S cm^{-1} at room temperature [82].

A different approach is the modification of commonly used Nafion membranes by incorporating different cations through a proton exchange mechanism between the membrane and the ionic liquids. Martínez de Yuso [83] studied the effect of the incorporation of n-dodecyltrimethylammonium (DTA$^+$) in protonated Nafion 112 membranes. An equilibrium value of 68% for the DTA$^+$ incorporation was obtained after 22 h of contact between the membrane and the IL solution. The contact angle studies showed a reduction in the hydrophobic character of the Nafion 112/DTA$^+$. The X-ray photoelectron spectroscopy (XPS) and thermogravimetric data showed a higher thermal stability and a lower water loss for modified samples heated at 120 ºC. The electronic changes in the Nafion 112 membrane were measured using electrochemical impedance spectroscopy (EIS), showing that replacing H$^+$ ions with DTA$^+$ cations increases the electrical resistance of the modified membrane. The methanol diffusion

was reduced approximately 2-fold when Nafion 112 and Nafion 112/DTA[+] were compared, benefitting DMFC applications. Diaz et al. [84] studied the performance of Nafion 112 membranes impregnated with different ionic liquids: 1-butyl-3-(4-sulphobutyl)-imidazolium trifluoromethanesulphonate ([HSO$_3$-BBIm][TfO]) and 1-methyl-3-(4-sulphobutyl)-imidazolium bis(trifluoromethylsulphonyl)imide ([HSO$_3$-BMIm][Tf$_2$N]). These ionic liquids contain an imidazolium cation due to its high electrochemical stability. Moreover, sulphonic groups were added to the cation to facilitate proton transport. Suitable anions, such as Tf$_2$N$^-$ and TfO$^-$, were selected due to their high ionic conductivity. Ionic liquids have a degradation temperature above 300 ºC, which made them suitable for fuel cell applications. The ionic liquid uptake in the membrane was evaluated through the weight difference between the pristine and the impregnated membrane. The [HSO$_3$-BBIm][TfO] and [HSO$_3$-BMIm][Tf$_2$N] uptakes were 9.4% and 1.6%, respectively. A higher current density was obtained when the Nafion membrane was impregnated with [HSO$_3$-BBIm][TfO], reaching 217 mA cm^{-2} without humidifying the inlet gases at 25 ºC. Di Noto and co-workers [85] studied the properties of Nafion 117 membranes doped with triethylammonium methanesulphonate (TMS) and triethylammonium perfluorobutanesulphonate (TPFBu). The water content of TPFBu is less than that of TMS due to its hydrophobicity, agreeing with the lower water content of Nafion doped with TPFBu relative to Nafion doped with TMS. The IL uptakes of the membranes impregnated with TMS and TPFBu were 20 and 39 wt%, respectively.

In the study developed by Langevin et al. [86] a composite proton-conducting membrane based on an ionic liquid and a porous polymer support was prepared for use in a PEMFC at elevated temperature. The composite material was prepared by impregnating a macroporous support with a highly proton conductive ionic liquid: triethylammonium trifluoromethanesulphonate (TFSu-TEA). These membranes showed conductivities of approximately 2.0 x 10^{-2} S cm^{-1} at 130 ºC and a storage modulus near 200 MPa at 150 ºC. Liew and co-workers prepared a proton conducting polymer electrolyte based on poly (vinyl alcohol)(PVA)/ammonium acetate (CH$_3$COONH$_4$)/1-butyl-3-methylimidazolium chloride (BmImCl) through a solution casting technique [87]. Ammonium acetate was used due its plasticising effect, while the ionic liquid was used to improve the ionic conductivity. As expected, the ionic conductivity increased with the mass loading of the ionic liquid. The increased ionic conductivity is due to the strong plasticising effect of the ionic liquid; this effect softens the polymer backbone, increasing the flexibility of the polymer chain that is important in order to improve Grotthus transport mechanism because this type of mechanism must be supported by short-distance transport of ions and it is promoted when the polymer chains have enough mobility. The ionic liquid also acts as a carrier of protons improving the ionic conduction trough vehicular mechanism. The highest ionic conductivity (5.74 x 10^{-3} S cm^{-1}) was achieved after adding 50 wt% BmImCl. A maximum power density of 18 mW cm^{-2} at room temperature was obtained in a PEMFC.

One of the most widely used polymers in polymer/ionic liquids blends is polyvinylidene fluoride (PVDF) and its copolymers [88-90]. Lee et al. [91] synthesised novel composite electrolyte membranes consisting of 1-ethyl-3-methylimidazolium fluorohydrogenates ([EMIm](FH)$_n$F) ionic liquids and the fluorinated polymers poly(decaflouorobiphenyl-(hexafluoropropylidene)diphenol) (s-DFBP-HFDP) and P(VDF-co-HFP). The ionic

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conductivity of the composite membrane P(VDF-co-HFP)/s-DFBPHFDP/[EMIm](FH)$_{2.3}$F with a weight ratio of 1/0.3/1.75 was 3.47 x 10^{-2} S cm^{-1} at 130 ºC. A single fuel cell exhibited an OCV of approximately 1 V at 130 ºC for over 5 hours. The polarisation curves under dry gases at 120 ºC were registered, showing a maximum power density of approximately 20.2 mW cm^{-2} at 60.1 mA cm^{-2}. Martinelli et al. [15] investigated the physical properties of proton conducting polymer membranes based on protic ionic liquids (EImTf$_2$N) incorporated into a polymer matrix (PVDF-co-HFP). The thermomechanical stability of the membrane improves when increasing the polymer concentration. However, there is an associated decrease in the conductivity due to the morphology of the membrane and possible interactions between the conducting IL and the polymer matrix. For the highest ionic liquid content, 80 wt%, the conductivity approaches the value of the pure ionic liquid, which is of the order of 1.0x10^{-2} S cm^{-1} at room temperature. Mališ et al. [92] prepared membranes consisting of a polymer and ionic liquid using the casting solution technique. Poly(vinylidene fluoride-co-hexafluoropropene) and Nafion were selected as the polymer matrix, while 1-butyl-3-methylimidazolium trifluoromethanesulphonate (BMImTfO) and 1-ethylimidazolium trifluoromethanesulphonate (EImTfO) were used as aprotic and protic ionic liquids, respectively. These composite membranes were tested in a PEMFC from 90-160 ºC with a humidified H$_2$ stream and compared with a PBI membrane as reference. The conductivity test showed that adding water to the IL increases the conductivity, particularly for [EIm][TfO]; adding 5 wt% water increased the conductivity by 170% (1.35 x 10^{-2} S cm^{-1}). This can be explained by the interaction between the water molecules and the ionic liquid. The existence of an ionic solvation shell induced by water encourages ion transport. Moreover, adding water increases the concentration of the charged carriers in the IL. In a humidified atmosphere, the highest conductivity was shown by Nafion/[BMIm][TfO] most likely due to the weaker interactions between [BMIm][TfO] and the polymer. Under dry conditions, the highest conductivity was observed for the membrane [EIm][TfO]/PVDF-co-HFP because the interactions between the IL and polymer were hindered, allowing the IL to keep water in its structure, thus ensuring high conductivity. The performance of these membranes in a fuel cell was significantly lower than that for the PBI membranes. The EIS test showed that these membranes had a high ohmic resistance between 1 and 12 Ω, while the PBI membrane had a resistance of 0.02 Ω. Another reason for the lower performance is the high resistance at the interface between the polymer electrolyte and the GDE.

Commercially available polybenzimidazole (PBI) is the most extensively studied and utilised polymer in membranes doped with acids for high temperature applications due to its excellent thermal and mechanical stability. Eguizábal et al. [93] developed composite membranes based on ionic liquids encapsulated in large pore zeolites and PBI for high temperature proton exchange membranes. Adding 1-H-3-methylimidazolium bis(trifluoromethanesulphonyl)imide ([HMI][Tf$_2$N]) in commercial zeolites to a PBI casting solution has been utilised for high temperature PEMFC applications. The conductivity of this material outperforms pristine PBI most likely due to the presence of the HMI cations and Tf$_2$N ions on the external surface of the zeolite crystals. Both ions favour acid-base interactions with the H$_3$PO$_4$-PBI system and a Grotthuss type mechanism through the ionic liquid network. An ionic conductivity of 5.4 x 10^{-2} S cm^{-1} at 200 ºC was achieved with the optimal membrane composition. Van de

Ven and co-workers [94] used 1-H-3-methylimidazolium bis(trifluoromethanesulphonyl)imide as a conductive filler in PBI. The composite membrane reached a proton conductivity of 1.86 x 10^{-3} S cm^{-1} at 190 ºC. The performance of these membranes exceeds that of Nafion 117 at temperatures above 90 ºC. Power densities of 39 mW cm^{-2} were obtained at 150 ºC with H_2/O_2. The composite membranes based on H_3PO_4/1-methyl-3-propyl-methylimidazolium dihydrogen phosphate (PMIH$_2$PO$_4$)/PBI were developed by Ye and co-workers for use at high temperatures in PEMFCs, showing a proton conductivity of 2.0 x 10^{-3} S cm^{-1} at 150 ºC under anhydrous conditions; the conductivity rises when the membranes absorb some water vapour. The PMIH$_2$PO$_4$ ionic liquid may act as a proton transfer bridge, a plasticiser for PBI and an absorber and retainer of water and may interact with the hydrogen bonds in the system [95]. In the study developed by Liu et al. [96] an ionic liquid doped PBI membrane was synthesised for H_2/Cl_2 fuel cell. Diethylmethylammonium trifluoromethanesulfonate ([dema][TfO]) showed better electrode reaction kinetics in comparison with pyridine, imidazole and amine based ILs. PBI and [dema][TfO] were compatible and the hybrid membranes showed high stability and ionic conductivity (20.73 x 10^{-3} S cm^{-1} at 160 ºC).

Sulphonated poly(ether ether ketones) are known for having good thermal stability and high proton conductivity. Therefore, a composite membrane based on an alkylimidazolium phosphate ionic liquid and sulphonated poly(ether ether ketone) was prepared using a solution casting method and characterised by Raja Jothi et al. [97]. Dialkylphosphate-based ILs have a high hydrolytic stability and anhydrous proton conductivity. The thermal stability of SPEEK/IL composite membranes is higher than that corresponding to pristine membranes. Adding an IL to SPEEK enhanced the ionic conductivity, reaching approximately 3.0 x 10^{-3} S cm^{-1} at 145 ºC under anhydrous conditions when 50 wt% IL was incorporated into the polymer matrix. This membrane was tested in a fuel cell at various temperatures under non-humidified conditions. At 145 ºC, the OCV was 0.83 V, and the maximum power density was 203 mW cm^{-2}.

The preparation of IL-based polymer electrolytes depends strongly on the compatibility of the ILs and the polymer matrix. This obstacle may be overcome in some cases through the polymerisation of IL-based micro-emulsions. Micro-emulsions are thermodynamically stable dispersions containing two immiscible liquids stabilised by surfactants at the liquid-liquid interface. Consequently, Yan et al. [98] prepared proton conducting membranes by polymerising micro-emulsions consisting of surfactant-stabilised protic ionic liquid nano-domains dispersed in a polymerisable mixture of styrene and acrylonitrile. Under non-humidifying conditions, the produced membranes have conductivities up to 1.0 x 10^{-1} S cm^{-1} at 160 °C due to the well-connected PIL nano-channels formed in the samples. However, the long-term operation of the PIL-based membranes might be affected by a progressive release of the PIL. Similarly, Chu and co-workers [99] developed anhydrous proton conducting membranes via in situ cross-linking of polymerisable oils (styrene/acrylonitrile) containing polyamidoamine (PAMAM) dendrimer-based macromolecular protic ionic liquids. The macromolecular PIL-based membranes show a proton conductivity of 1.2 x 10^{-2} S cm^{-1} at 160 ºC and have better PIL retention than those containing small-molecule PILs.

Sulphonated polyimides are polymers with good film-forming properties and a high thermal stability. They can be blended with ionic liquids to form highly proton-

conductive electrolytes. Watanabe and co-workers have studied ionic liquid/sulphonated polyimide composite membranes for non-humidified fuel cells [81, 100, 101]. The protic ionic liquid [dema][TfO] exhibits high thermal stability and high ionic conductivity at 120 ºC under anhydrous conditions and can be used as a proton conductive electrolyte in H_2/O_2 fuel cells. These membranes have proton conductivities of approximately 1.0×10^{-2} S cm^{-1} at 120 ºC. A maximum current density of 250 mA cm^{-2} and a peak power density of 63 mW cm^{-2} were obtained; the gas permeability was comparable to humidified Nafion membranes. In a different work developed by Yasuda and Watanabe SPI/[dema][TfO] membranes were tested in a fuel cell at 120 ºC under anhydrous conditions. An aging process was utilised because [dema][TfO] could leak out, acting as an ion conductor layer and forming a three-phase boundary layer in the catalyst. Maximum current densities and power densities of approximately 400 mA cm^{-2} and 100 mW cm^{-2} were obtained, respectively. Increasing the gas flow rate decreased the fuel potential, probably due to the unstable three-phase boundary layer in the catalyst formed by the leaked [dema][TfO] which is strongly affected by the environment [102].

The morphology of the IL-incorporating polymers is important to consider when attempting to improve the transport properties. Some studies showed that membranes exhibiting phase-separated morphologies present better conductivity values. The type of cations and anions is an important factor when determining the morphologies of the polymers due to the interactions between the ILs and the polymer backbones [61].

Imidazolium ionic liquids have been the most investigated ILs. However, most of these electrolytes can only provide rather low fuel cell performance. This poor performance usually is attributed to several causes such as the test station, fuel cell structure and low conductivity of the composite membrane. However, little attention has been paid to the influence of ILs and their impurities on the catalyst activity. Gao and co-workers [103] have studied the influence of cations of ILs on Pt/C catalyst by cyclic voltammogram. It was found that imidazolium cation results in smaller electrochemical active surface areas (EAS) of Pt/C than those of trimethylethyl amide and pyridinium. This decrease is believed to cause significant fuel cell performance decrease. Besides, in another study developed by Gao et al. [104] an imidazolium ionic liquid, ethylmethyl imidazolium hydrosulphate ([Emim]HSO_4), was synthesized by different precursors with various amounts of Br impurity and its effect on Pt/C catalyst toward oxygen reduction reaction (ORR) was investigated. The results show that Br^- can cause drastic performance decrease of Pt/C for ORR. The reason is that Br^- suppresses both the initial adsorption of O_2 molecule and the formation of platinum site pairs necessary for the cleavage of the O-O bond.

Table 2 summarizes the published works concerning ionic liquid/polymer blends. Different works have remarked the advantages of using ionic liquids as membrane electrolytes in fuel cells over the last few years. However, the optimal way for ionic liquids to form a solid membrane is still unclear. One of the studied possibilities is the polymerisation of blends consisting of common monomers and ionic liquids. Nevertheless, this technique results in a compromise solution between the mechanical stability and proton transport properties. PVDF and its derivatives have been widely studied in IL membrane polymerisation because they have excellent mechanical stability. These polymers can provide the stability required for fuel cell membranes

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whereas the ionic liquid is the responsible for the proton transport. The use of micro emulsions is a good alternative in order to avoid phase separation and encourage the compatibility between monomer and ionic liquid. The majority of the studies dealing with blends of ionic liquids and polymers are limited to the characterization of the membrane in terms of conductivity. It is essential the membrane testing in real fuel cell system because variables such as the mechanical strength can influence the performance of these devices. The stability of the new membranes must be assessed through long term experiments in order to offer an adequate alternative to the most commonly used Nafion membranes.

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Table 2. Ionic liquid/Polymer blends

Membrane	Conductivity	Remarks	References
EMImTf$_2$N/TMOS/MTMOS/PO(OCH$_3$)$_3$	5.4 x 10^{-3} S cm^{-1} at 150 °C	High chemical and thermal stability with power density of 0.22 mW cm^{-2} at 0.47 mA cm^{-2}. The maximum current density was 0.76 mA cm^{-2} at 150 °C under anhydrous conditions	73
MPnTf$_2$N-MPzTf$_2$N-MPyTf$_2$N-MImTf$_2$N-EImTf$_2$N/PVdF	1.0 x 10^{-2} S cm^{-1} at 140 °C EImTFSI	Thermally stable	88
SPEEK/BMImBF$_4$	1.04 x 10^{-2} S cm^{-1} at 170 °C	The influence of the solvent has been studied. DMF generates ionic clusters in the membrane that facilitate proton transport	105
MMA/BMImPF$_6$	2.0 x 10^{-4} S cm^{-1}	The resulting polymer gels were flexible, transparent and highly conductive films	106
PAN-PEO-PVA-TMS/BMPIm-BMImPF$_6$-EMImBF$_4$	6.6 x 10^{-3} S cm^{-1} PAN/EMIBF$_4$	Membranes with TMS were more flexible while exhibiting improved mechanical strength and conductivity	107
PM-DPGDA-AU-DDA/EMImBF$_4$-EMImTf$_2$N-BMImBF$_4$-EMImTf$_2$N-BMPyTf$_2$N	DDA/EMImBF$_4$ 1.8 x 10^{-2} S cm^{-1}	The conductivity values of the obtained solid electrolytes were comparable to that of the ILs used as electrolytes	108
EMPyr(FH)F/HEMA	8.19 x 10^{-2} S cm^{-1} at 100 °C	Power density of 32 mW cm^{-2} at 50 °C under non-humidified condition. The performance deteriorated beyond 80 °C due to the blockage of gas channels in the GDEs	109
MA-acrylonitrile-vinyl acetate-styrene-HEMA/EMIBF$_4$-BPBF$_4$	BPBF$_4$/HEMA 1.0 x 10^{-3} S cm-1 at 30 °C	Most of the resulting polymers were incompatible and formed separate phases with EMIBF$_4$ or BPBF$_4$. Poly(HEMA) showed a comparatively good compatibility, and the mixtures after polymerisation gave translucent gels	110
EMImTF$_2$N/MMA-acrylonitrile-vinyl acetate-styrene-HEMA-MA- acrylamide	1.0 x 10^{-2} S cm-1 at 30 °C	MMA and MA were compatible with the IL. Ionic gels showed high ionic conductivities at room temperature and presented sufficiently high mechanical strength, transparency and flexibility	111

Nafion/TMPA⁺ Cl⁻; DTA⁺ Cl⁻; CTA⁺ Br⁻; BMIm⁺PF₆⁻; OMIm⁺PF₆⁻	Nafion/DTA⁺:4.0 x 10⁻⁶ S cm⁻¹; Nafion/CTA⁺:7.0 x 10⁻⁷ S cm⁻¹	Possibility to design membranes with either higher or lower ionic conductivity depending on the cation incorporated	112
Nafion/TMA⁺ Cl⁻; BMIM⁺ Tf₂N⁻; OMIM⁺ Tf₂N⁻; ALIQUAT⁺ DCA⁻; TMPA⁺ Cl⁻; DTA⁺ Cl⁻CTA⁺ Br⁻		Methanol and gas crossover were reduced in comparison to Nafion 112	113

3.3. POLYMERISED IONIC LIQUID MEMBRANES

The most innovative technique used to generate solid polymeric electrolytes from ionic liquids is the polymerisation of ionic liquids containing vinyl groups. Polymerised ionic liquids (PILs) include a wide variety of structures; they can be designed to form different systems, such as polycationic ILs, polyanionic ILs, polymer complexes, copolymers and poly(zwitterion)s, depending on the final application of the polyelectrolyte (figure 7) [114] .

PILs can be synthesised through two basic strategies: the direct polymerisation of IL monomers and the chemical modification of existing polymers [115]. The polymerisation of IL monomers is a widely adopted method to prepare PILs. Free radical polymerisation is a largely used method due to its high tolerance toward impurities, moisture and other functional groups. The most commonly used IL monomers in free radical polymerisation have (meth)acryloyl, styrenic and N-vinylimidazolium groups. Recently, PILs have been prepared via controlled radical polymerisation, revealing an opportunity to design and control the macromolecular architecture of the IL species. Atom transfer radical polymerisation (ATRP) and reversible addition-fragmentation chain transfer polymerisation (RAFT) have been used to prepare homopolymers and block copolymers of ILs. Another simple and intuitive method used to prepare PILs is photopolymerisation. Noble and co-workers reported the formation of PILs and PIL-IL composites via the photopolymerisation of an imidazolium-based monomer with excellent properties as gas separation membranes [116-119]. PILs can be developed through the chemical modification of existing polymers. When using this strategy, the formed PIL will adopt varying degrees of polymerisation and the structure of the original polymer. Two main paths can be used to accomplish the modification: grafting N-alkyl imidazoles onto the halo-alkyl function present in each repeating unit of polymers and reacting halo-alkane with polymers containing imidazole [115].

The ionic conductivities of ILs are usually on the order of 1.0×10^{-2} S cm^{-1} depending on their chemical nature. However, PILs are below 1.0×10^{-6} S cm^{-1}. After polymerising the IL monomers, the ionic conductivity drops due to the increase in glass transition temperature and the decrease in the number of mobile ions and their mobility. The ionic conductivity of PILs can be enhanced by two strategies: by increasing the concentration of the carrier ions and increasing the mobility of ions by modifying the structure of the electrolyte. In the study carried out by Põhako-Esko et al. [120] both strategies mentioned above were combined in order to develop a new type of composite material by adding the non-polymerisable ionic liquid 1-ethyl-3-methyl imidazolium tetrafluoroborate ([EMIM][BF$_4$]) to different methacrylate-types PILs. An increase in [EMIM][BF$_4$] content in the composites led to an increase in the ionic conductivity of the materials. The 40% vol/vol composites had conductivities of approximately 1×10^{-4} S cm^{-1} compared to the conductivities of 1×10^{-5} S cm^{-1} for the corresponding neat PIL. Above this [EMIM][BF$_4$] content the materials were sticky gels. Marcilla and co-workers [121] synthesised a new type of tailor-made polymer electrolyte based on ionic liquids and polymeric ionic liquids analogues by mixing 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonimide) [bmim][Tf$_2$N], 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF$_4$] and 1-butyl-3-methylimidazolium

bromide [bmim][Br⁻] with poly(1-vinyl-ethyl-imidazolium) bearing similar counter-anions [Tf$_2$N],[BF$_4$] and [Br⁻]. The chemical affinity between PILs and ILs allows a completely compatible combination resulting in stable polymer electrolytes. The ionic conductivity of all these electrolytes varies between 1 x 10^{-2} S cm^{-1} and 1 x 10^{-5} S cm^{-1} at room temperature and, at high IL contents the ionic conductivity reached values close to the values of the IL compounds although the mechanical stability was compromised. Moreover, adequate anions and cations must be chosen for the ion conduction depending on the final application because every electrolyte has the optimum performance for a specific type of electrochemical device [122, 123].

Various authors have studied the polymerisation of ionic liquids for electrochemical applications. Li et al. [124] synthesised a series of guanidinium polymeric ionic liquid electrolytes for lithium batteries. To combine the good electrochemical properties of ILs with the film-forming capabilities of polymers, guanidinium IL with different anions, such as BF$_4$⁻, PF$_6$⁻, ClO$_4$⁻ and Tf$_2$N⁻, was prepared via copolymerisation with methyl acrylate and an anion exchange reaction with the lithium salt. The properties of the polymeric membranes depend on the anionic species; these structures possess good thermal stability and a high ionic conductivity. The membrane with the BF$_4$⁻ anion displays the best thermal stability and decomposes at 353 ºC. The best ionic conductivity was 1.35 x 10^{-4} S cm^{-1} at 30 ºC. Green et al. [125] developed a series of polyelectrolytes based on vinylimidazolium homopolymers with different lengths of alkyl substituents and anions through conventional free radical polymerisation. After an anion exchange with BF$_4$⁻, TfO⁻ or Tf$_2$N⁻, the solubility, thermal properties and thermal stability were modified. These anions increased the relative hydrophobicity, generating water insoluble homopolymers. Longer alkyl chain lengths decreased the Tg for Br⁻ and BF$_4$⁻ anions, while TfO⁻ and Tf$_2$N⁻ decreased from ethyl to butyl substituents and increased from butyl to octyl substituents. Increasing the length of the alkyl substituents decreased the thermal stability. Exchanging the Br⁻ anion to BF$_4$⁻, TfO⁻ or Tf$_2$N⁻ reduced the Tg and increased the thermal stability due to the low basicity. The ionic conductivity was higher for imidazolium homopolymers with the Tf$_2$N⁻ anion. The synthesis, thermal characterisation and ionic conductivity of styrenic imidazolium ionic liquid homopolymers with different counter-ions were described by Weber et al. [126]. They found that the ionic conductivity increased 2-3 times as the temperature increased from 80 to 150 ºC for all hydrophobic PILs (Tf$_2$N⁻, BF$_4$⁻ and PF$_6$⁻ counter-anions). Higher ionic conductivities were achieved with the Tf$_2$N anion. The differences in conductivity appear to be caused by differences in the Tg and the consequent temperature dependence in the segmental motion of the polymer chain. However, the ionic size and symmetry also influence the intrinsic ionic conductivity of the PIL homopolymers. The ionic conductivity of the hydrophilic PILs was evaluated. In contrast to the hydrophobic PILs, where the ionic mobility depends mainly on the segmental dynamics of the polymer chain, the ionic conductivity in solvated hydrophilic PILs depends on the water content, allowing solvent-assisted transport.

Ohno and co-workers prepared various polymeric ionic liquid systems with different structures, and their ion transport properties have been studied. The polymerisation of ionic liquids induced a considerable decrease in the mobility of ions in the matrix due to the increased glass transition temperature [114]. Consequently, they studied the influence of a spacer placed between the main polymer chain and the anionic charge.

Yoshizawa et al. [127] developed ionic liquid polymers with a flexible spacer poly(vinylimidazolium-co-3-sulphopropyl acrylate). They measured the ionic conductivity as 1.2×10^{-5} S cm^{-1} at 50 ºC, surpassing than that of the polymer without the spacer (1.0×10^{-9} S cm^{-1} at 50 ºC). The effect of the position of the imidazolium cations and the spacer structure on the ionic conductivity of a series of polymerisable ionic liquids has been studied [128]. Polycation-type ILs with flexible long spacers have the same conductivity as polyanion-type ionic liquids without spacers, 1.0×10^{-4} S cm^{-1} at room temperature. Therefore, the freedom of the imidazolium cation strongly affected the ionic conductivity. Because the ionic conductivity is a function of Tg, it is important to lower Tg to enhance the ionic conductivity in the polymerised ionic liquids. In this case, both systems maintained reasonably low glass transition temperatures (approximately -60 ºC) after polymerisation. Similar effects were observed in a different study by Ohno [129]. In order to minimise the drop in conductivity, when molten salts are polymerized the vinyl group and the molten salt unit were tethered with oligo(ethylene oxide), improving the ionic conductivity 300 times at 25 ºC.

The effect of adding a crosslinking agent was investigated by Washiro et al. [130]. In this study, ionic liquid-type polymer brushes with different hydrocarbon chain lengths between the polymerisable group and the imidazolium ring were synthesised. The polymer synthesised with a hexamethylene spacer chain and an ethylimidazolium cation (P(EITH$_6$A)) showed the highest conductivity (up to 1.0×10^{-4} S cm^{-1} at 30 ºC) and a lower Tg (-59.1 ºC). These polymers are thermally stable up to approximately 400 ºC. The mechanical strength of these polymers was improved by crosslinking with tri(ethylene glycol) divinyl ether. Large amounts of the cross-linker reduce the conductivity because the motion of the polymer backbone is restricted and Tg increases. The transparent and flexible film with the highest ionic conductivity (1.1×10^{-4} S cm^{-1} at 30 ºC) was obtained with 0.5 mol% tetra(ethylene glycol)diacrylate cross-linker, remaining equivalent to that of the system before polymerisation. An appropriate ethylene oxide (EO) spacer length and a polymerisable group were required to maintain the high segmental motion of the matrix. The synthesis and polymerisation of cross-linking monomers based on ionic liquids was investigated to obtain thermally stable polymers with a high ionic conductivity [80]. The copolymerisation of mono acrylic-type ionic liquid monomer with a new cross-linker generated a polymer with high ionic conductivity, 1.36×10^{-4} S cm^{-1} at 50 °C. This networked polymer had a good thermal stability at approximately 400 ºC. The copolymerisation of the mono-acrylate monomer with the cross-linking monomer in the presence of an ethylimidazolium ionic liquid produced films with a high ionic conductivity and a very high thermal stability. Imidazolium-type ionic liquids containing two vinyl groups were synthesised by Ohno [114] as an IL type cross-linker for improving the mechanical properties without lowering the ionic density, even after polymerisation.

The effect of adding salts to the monomer on the ionic conductivity has also been studied. Yoshizawa et al. prepared copolymers through the radical polymerisation of 1-vinylimidazole neutralised with acids containing a vinyl group. When an equimolecular amount of lithium bis(trifluoromethane sulphonyl)imide salt (LiTf$_2$N) was added to the poly(vinylimidazolium-co-vinylsulphonate), the ionic conductivity was 7.2×10^{-7} S cm^{-1} at 50 ºC, while the ionic conductivity of the copolymer without the salt was below 1.0×10^{-9} S cm^{-1} at the same temperature [127]. Ohno studied the effect of adding salt to

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polymerised N-vinyl-3-ethylimidazolium trifluoromethanesulphonylimide (EVImTf$_2$N). The ionic conductivity dropped 100 times after polymerisation. Adding low molecular weight salts was effective for improving the performance of the ion-conductive polymers. However, the ionic conductivity increased only slightly because adding salt is generally effective only when the matrix has moderate ion conductivity [129]. Nakajima and Ohno investigated the effect of adding ethylmethylimidazolium (EMI) salts to improve the ionic conductivity of the polymers. Therefore, different salt concentrations were added to 1-[2-(acryloyloxy)ethyl]-3-ethylimidazolium bis(trifluoromethanesulphonyl)imide in the presence of a cross-linking monomer containing an ionic liquid moiety. The ionic conductivity increased when increasing the amount of EMIBF$_4$. The polymer without EMIBF$_4$ was an anionic conductor because all of the cations were fixed to the main chain. After adding the imidazolium salt, it became a bi-ionic conductor. The ionic conductivity exceeded that of the monomer (3.63 x 10^{-3} S cm^{-1} at 50 ºC) when 200 mol% EMIBF$_4$ was added [80].

Shaplov and co-workers utilised four ionic monomers with quaternised cations to obtain high molecular mass PILs: N-[(2-Methacryloyloxy)propyl]-N-methylpyrrolidinium bis-(trifluoromethylsulphonyl)amide (M1), 1-[2-(methacryloyloxy)propyl]-3-methylimidazolium bis-(trifluoromethylsulphonyl)imide (M2), N-methyl-N-ethylpyrrolidinium(3-sulphopropyl) methacrylate (M3) and 1-methyl-3-ethylimidazolium(3-sulphopropyl) methacrylate (M4). The free radical polymerisation could be optimised. The optimal azobisisobutyronitrile (AIBN) concentration (0.5 wt%), monomer concentration ([solvent]/[M]=1:1 by wt%) and reaction time (6 h.) were similar for both polycations and polyanions. The reaction media was different; for the polycations, the best reaction medium was an ionic liquid with the same anion as the monomer, while for the polyanion, the best reaction medium was 1,1,1,3,3,3-hexafluoroisopropanol (HFIP). The ionic conductivity of polycation PIL1 was 7.8 x 10^{-9} S cm^{-1} at 25 ºC, while for polyanion PIL3, the value reached 3.3 x 10^{-10} S cm^{-1}. This behaviour can be explained by the poor dissociation of the bulky pyrrolidinium cation and the inactivated SO$_3^-$ groups compared to the small and highly delocalised TFSI anion. The ionic conductivities of polycation PIL2 and polyanion PIL4 were similar (3.1 and 3.2 x 10^{-8}, respectively), most likely due to the delocalisation of the imidazolium cation. The Tg of the studied polyelectrolytes exceeds 25 ºC, except for PIL2 (Tg = 16 ºC). The conductivity was improved, and the Tg was lowered through the copolymerisation with poly(ethylene glycol) dimethacrylate (PEGDM). The copolymerisation with PEGDM lowered the Tg and increased the ionic conductivity (10-1000 times higher than that of respective homopolyelectrolytes) [131].

Mel'nik et al. [132] studied the influence of incorporating bulky diethoxyphosphoryl groups into the said chains of polymers through the free-radical polymerisation of vinyl imidazolium ionic liquid monomers. Introducing dihydroxy and diethoxyphosphoryl groups into the side chain of the polycation decreased the Tg of the polymers. Nevertheless, a higher thermal stability was displayed by polymers containing less bulky alkyl side substituents. Chen and co-workers [133] synthesised two different random copolymers through free-radical polymerisation. The first copolymer consists of an ionic monomer (1-[2-methacryloyloxyethyl]-3-butylimidazolium tetrafluoroborate (MEBIm-BF$_4$)) and a non-ionic monomer (hexyl methacrylate (HMA)). The second copolymer consists of the same ionic unit as the first copolymer, but the

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tetrafluoroborate anion was exchanged with bis(trifluoromehtylsulphonyl)imide anions (Tf$_2$N). Poly(HMA-co-MEBIm-BF$_4$) copolymers have an onset temperature of 237 ºC, while replacing the BF$_4$ anion with a Tf$_2$N anion improved the thermal stability, reaching an onset temperature of 373 ºC. The ionic conductivity of poly(HMA-co-MEBIm-BF$_4$) increased with the temperature from 1.0 x 10^{-6} S cm^{-1} to 1.0 x 10^{-4} at 150 ºC. The ionic conductivity increased by over an order of magnitude when increasing the HMA composition because the Tg was lowered. For the ionic-ionic copolymer, the conductivity increased with the Tf$_2$N content because this large anion resulted in weaker interactions and reduced the Tg.

Despite the noteworthy increase in the publications about polymeric ionic liquids for electrochemical applications, few studies have tested these membranes in a real fuel cell system. Diaz et al. [84] designed task-specific protic ionic liquid monomer for use as electrolyte in fuel cells. In that work, an imidazolium cation was chosen for its high electrochemical stability. Moreover, sulphonic groups were incorporated into the cation as side chains, improving the proton transport. The TfO$^-$ anion provides a high ionic conductivity. The chemical structure of the IL monomer is shown in figure 8. The polymeric ionic liquid was obtained through a photopolymerisation of the ionic liquid monomer: 1-(4-sulphobutyl)-3-vinylimidazolium trifluoromethanesulphonate ([HSO$_3$-BVIm][TfO]). This material was tested directly as the electrolyte without humidifying the inlet gases. This polymerised IL reached current densities of approximately 154 mA cm^{-2} at 25 ºC and peak power densities of approximately 33.1 mW cm^{-2}. The molecular dynamics and ions transport properties of poly([HSO$_3$-BVIm][TfO]) were investigates by Z. Wojnarowska et al. [134]. The results analyzed in complex electrical modulus $M^*(f)$ and complex conductivity $\sigma^*(f)$ formalisms have revealed a fundamental difference between the conducting properties of the polymer membrane and its low-molecular weight counterpart. The large decoupling between the conductivity relaxation times and segmental dynamics observed for poly([HSO$_3$-BVIm][TfO]) in the vicinity of Tg is an evidence that the conductivity of the studied PIL is controlled by the fast proton hopping via the hydrogen bond network, in contrast to the monomer where the diffusion of cations and anions is relevant. The influence of water on the relation between conductivity relaxation times (τ_σ) and segmental dynamics (τ_α) of the PIL was evaluated. The dependence of conductivity relaxation times with temperature is influenced by the water content. This effect is clearly visible in the value of Tg, which decreases almost 80 K with an increase of the water fraction from 1.96 to 11.14 wt%.

Polymerized ionic liquids constitute an important innovation in the field of electrolyte membranes because they can be used directly as polymeric solid membranes replacing conventional perfluorinated membranes. The tunability of ionic liquids permits the synthesis of ionic liquid polymers with different morphologies and specific properties. However, it is well known that the conductivity of the ionic liquid drops significantly when it is polymerised. To overcome this issue, one strategy is the incorporation of a spacer placed between the main polymer chain and the anionic charge. The freedom of the ion responsible for the proton conduction is a key factor, as it was demonstrated in polyanions with imidazolium cations. Another strategy already considered in order to reduce the drop in conductivity after polymerisation is the addition of non-polymerisable additives to the ionic liquid monomer. This technique provides fluidity to the polymer improving the proton transport. The main drawback of

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polymerised ionic liquids is the mechanical stability that could be improved through the addition of an appropriate crosslinker. However, the proton conductivity would be reduced. As in the case of polymer/ionic liquid blends, most publications deal with the characterization of these materials and only few of them test the membrane in a fuel cell system. It is still necessary to continue working on the development of polymerised ionic liquid membranes with high proton conductivity and enough mechanical stability for a real fuel cell application.

3.4. ORGANIC IONIC PLASTIC CRYSTAL ELECTROLYTES

Plastic crystals are promising materials that form a novel class of solid electrolytes due to their unique properties. There are two general classes of organic plastic crystals: molecular plastic crystals, such as succiononitrile [135-137], and organic ionic plastic crystals (OIPCs). Plastic crystals were first revealed by Timmermans in the 1960s, who described a number of relevant features of plastic crystalline behaviour, such as a low entropy of melting ($\Delta Sf<20$ J/Kmol) [138]. OIPCs are a family of solid state electrolytes with electrochemical applications. Their negligible volatility and high thermal and electrochemical stability make them suitable solid electrolytes in many electrochemical devices, such as lithium batteries, dye-sensitised solar cells and fuel cells [139-143].These materials have the advantages of ILs (high proton conductivity without humidification) and the benefits of a solid state electrolyte, making them promising new proton conductive electrolytes for fuel cells.

OIPCs are usually formed from a large symmetric organic cation and an inorganic anion that is normally symmetrical or has a diffusive charge. These materials have one or more solid-phase transitions before melting that are associated with the beginning of rotational or translational motions of the ions. This translation leads to a progressive transformation from an ordered crystalline phase to an increasingly disordered structure. The highest temperature solid phase is denoted phase I; the lower temperature phases are phases II, III, etc. The conductivity of these materials is attributed the presence of defects or vacancies in the crystalline structure, the rotational and translational disorder of the cation and anion and the conformational disorder of the ions [144]. These materials are referred to as "plastic crystals" due to their softness; they are easily deformed under stress. This deformation occurs due to the mobility of the slip planes, dislocations or vacancy migrations. These properties are beneficial for fuel cell devices because they should suffer less from any loss of contact with the electrodes due to volumetric changes [66]. Plastic crystals are usually used as matrix materials for adding dopant ions, such as Li^+ for lithium batteries or I^-/I_3^- for dye-sensitised solar cells, significantly increasing the ion conductivity.

There are lots of challenges concerning OIPCs. The mechanisms responsible for their proton conduction are not clearly understood. The relationship between the chemical structures of the ions and the physical properties of the resultant salt remains unclear. Finally, the development of solid state electrolytes from these materials is in its early stages [138].

Different OIPC systems have been studied for their use as electrolytes in fuel cells. Choline dihydrogenphosphate [choline][DHP] was studied for the excellent proton conductivities of the phosphoric acid base materials. The proton transport of this material might be facilitated by a triple rotation of the dihydrogenphosphate anion. High proton diffusivities can be obtained after doping with acid. The thermal stability of [choline][DHP] doped with phosphoric acid is good, with minimal weight loss up to 200 ºC. However, this OIPC with 18 mol% phosphoric acid presents an amorphous phase. In contrast, using 4 wt% triflic acid or Tf_2N acid improves the conductivity without deforming the crystalline structure. Moreover, [choline][DHP] doped with 4 mol% triflic acid generated significant proton reduction currents, which is an important feature for fuel cells [144]. Yoshizawa-Fujita [145] synthesised choline dihydrogen phosphate $[N_{1,1,1,2OH}][DHP]$ and 1-butyl-3-methylimidazolium dihydrogen phosphate $[C_4mim][DHP]$ as new proton-conducting ionic plastic crystals (figure 9). $[C_4mim]DHP]$ showed solid-solid phase transitions and a melting point at 23 and 119 ºC, whereas $[N_{1,1,1,2OH}][DHP]$ displayed solid-solid phase transitions and melting points at 45, 71 and 167 ºC. Ionic conductivities ranging from 1.0×10^{-6} to 1.0×10^{-3} S cm^{-1} for choline dihydrogen phosphate and to 1.0×10^{-5} S cm^{-1} for 1-butyl-3-methylimidazolium dihydrogen phosphate were achieved in the plastic crystalline phase. $[N_{1,1,1,2OH}][DHP]$ showed one order of magnitude more ionic conductivity than $[C_4mim][DHP]$ in phase I, revealing that the hydroxyl group is suitable for fast proton transport in the solid state.

Proton conducting membranes based on impregnated cellulose acetate supports with mixtures of choline dihydrogen phosphate and various acids were synthesised by Rana et al. [146]. The 18 mol% H_3PO_4-containing [choline][DHP] membrane was tested in a fuel cell at 120 ºC under non-humidified conditions. The open circuit voltage was zero, possibly due to the poor hydrogen oxidation reaction and oxygen reduction reaction kinetics at the electrode interface. A membrane doped with 4 mol% $HNTf_2$ was also tested, giving zero OCV with the dry membrane at 125 ºC. Nevertheless, a wet membrane containing up to 50 wt% water showed an OCV of approximately 0.78 V. The impedance of the cell was approximately 3 Ω under operational conditions. On the other hand, solid-state organic ionic plastic crystal - polymer nanofiber composite electrolytes were described for the first time for lithium batteries applications. The new composite materials exhibited enhanced conductivity, excellent thermal, mechanical and electrochemical stability and allow the production of optically transparent, free-standing, flexible and thin film electrolytes (10's μms thick) [147].

The proton transport behaviour in the guanidinium triflate (GTf) solid and its mixtures with triflic acid was studied by Zhu and co-workers [148]. Both the pure GTf and 1 mol% doped samples showed relatively low conductivity and strong temperature dependency. Nevertheless, for the samples containing 2 mol% acid or more, the conductivities are high (1.0×10^{-3} S cm^{-1}) and relatively independent of temperature. For all the measured temperatures, an increase in the conductivity can be found between the acid contents of 1-2 mol%. This behaviour is a strong indication of percolation-dominated conducting mechanisms of the system. However, at high temperatures the GTf matrix also becomes conductive and contributes to the conductivity of the composites. In the study carried out by Adebahr et al. [149] the thermal characteristics, as well as the rotational and translational properties of dimethylpyrrolidinium thiocyanate were evaluated. This plastic crystal changes from a

rigid networked structure in phase II to allow the isotropic tumbling of the cations in the plastic phase (phase I). Raman measurements reveal the rotational motions of the cations and anions. An increase in conductivity was observed at the phase II → I and I → melt transitions, suggesting that the increase in the free volume and larger voids due to the rotational motions of the ions causes cation and anion translational diffusive motions. The structure and transport of N-propyl-N-methylpyrrolidinium tetrafluoroborate has been investigated by Efthimiadis and co-workers [150]. The ionic conductivity in the plastic crystal phase is comparable to that in the melt (1.0×10^{-3} S cm^{-1}) due to the high defect concentration associated with the onset of orientational disorder. Scanning electron microscopy suggested a complex surface morphology and lattice imperfections associated with the strong orientational disorder of the plastic state.

Plastic crystals are a novel class of solid electrolytes. There are still few publications on this topic in literature. To the best of our knowledge the best option to use OPICs as solid membranes is through the use of polymeric nanofibers supports impregnated with the plastic crystal doped with strong acids. However, further studies are necessary with the aim of better understanding their proton transport properties and their performance in fuel cell devices.

4. ELECTROLYTES FOR FUEL CELL APPLICATIONS: AN OVERVIEW

Table 3 compares the electrolytes studied in this review. Toward this purpose, the most relevant results have been classified according to their composition, highlighting the main obtained conclusions.

Nafion is a polymer with excellent mechanical and thermal properties and outstanding conductivities when it is well hydrated. However, using Nafion is not feasible at temperatures above 80 ºC because of the evaporation of water. Consequently, several works are related to the modification of Nafion membranes toward improving their water retention. Zeng and co-workers [151] developed Nafion membranes with silica for PEMFCs without humidification. These membranes have conductivities of approximately 1.11×10^{-1} S cm^{-1} at 25 ºC, allowing an increase of approximately 30% in the fuel cell performance.

To reduce the cost of the perfluorinated membranes, partially fluorinated membranes are being studied by many researchers. PFA/PTFE membranes were developed by Muto et al. [9]. A high conductivity of 1.7×10^{-1} S cm^{-1} at 60 ºC was obtained, and power densities of approximately 630 mW cm^{-2} at 60 ºC with humidified gases were reached. However, similar to the fluorinated membranes, these electrolytes need humidification for an optimal performance.

Non-fluorinated membranes are a cheap alternative PEM. However, as in previous cases, they require a proton conductor. Several authors have studied SPEEK membranes due to their availability and processability. Cross-linkable sulphonated poly(ether sulphone) had a conductivity of 1.2×10^{-1} S cm^{-1} at room temperature and a current density of 1500 mA cm^{-2} at 0.6 V in a PEMFC at 70 ºC with humidified gases

[19]. SPEEK/amino-functionalised silica membranes showed 1.0×10^{-1} S cm^{-1} at 120 ºC and peak power densities of 246 mW cm^{-2} at 120 ºC with humidified gases [30].

Acid-base blends are a promising PEM alternative due to their high conductivity, even under anhydrous conditions. Therefore, they are suitable for high temperature PEMFCs. PBI is a widely used polymer due to its excellent thermal and mechanical stability. When it is doped with a strong acid, it shows high anhydrous proton conductivity. However, the acid in these membranes can leach out, and the mechanical stability is decreased at high doping levels. PBI/H$_3$PO$_4$ membranes were developed by Li et al. [39], showing conductivities ranging from 2.5×10^{-2} - 6.8×10^{-2} at 200 ºC. These materials showed a peak power density of 1000 mW cm^{-2} in a PEMFC at 200 ºC without humidification.

Ionic liquids are attracting interest as a new class of PEM due to their exceptional properties, including their high anhydrous conductivity, negligible vapour pressure and high thermal and electrochemical stability. To use these compounds as electrolytes in PEMFCs, they must be in a solid film state. One approach involves mixing ILs with common polymers. Yasuda and co-workers [102] developed a SPI/[dema][TfO] membrane for PEMFCs under non-humidified conditions. This membrane reaches peak power density of 100 mW cm^{-2} and maximum current density of 400 mA cm^{-2} at 120 ºC. The conductivity increased with the [dema][TfO] content in the range between 1.0×10^{-4} – 1.0×10^{-2} S cm^{-1} at 120 ºC. However, this membrane has an unstable three-phase boundary in the catalyst layer formed by leaked [dema][TfO]. SPEEK/[EMIm][DEP] membranes were developed by Jothi et al. [97]. These membranes have a conductivity of 3.16×10^{-3} S cm^{-1} at 145 ºC and a maximum power density of 203 mW cm^{-2} at 145 ºC without humidification. Nevertheless, these membranes require improvements in their mechanical stability. Another approach toward generating solid ionic electrolytes is the polymerisation of ionic liquid monomers. The number of publications concerning polymeric ionic liquid has grown noticeably in recent years. However, few papers report testing these new polymers in a fuel cell system. In the work developed by Díaz et al. [84] the ionic liquid [HSO$_3$-BVIm][TfO] was polymerised and tested in a PEMFC at 25 ºC under anhydrous conditions, reaching a maximum current density of 154 mA cm^{-2} and a peak power density of 33.1 mW cm^{-2}. These membranes were thermally stable up to 300 ºC. The use of ionic liquids as conductive electrolytes membranes has achieved important improvements in terms of proton conductivity, thermal and electrochemical stability even at dry conditions. But still the main challenge of these compounds lays in selecting the most suitable molecular design of the ion pair which combines the entire requirements for the membrane electrolyte in a fuel cell including mechanical stability without compromising the proton transport activity.

Another promising approach is focused on the use of organic ionic plastic crystals which are a new family of solid state electrolytes suitable for fuel cell applications. Membranes based on cellulose acetate supports with [choline][DHP] doped with various acids were studied by Rana et al. [146]. Zero OCV in their dry states was obtained in a PEMFC at 80 ºC. However, when the electrolytes contained 50 wt% water, an OCV of 0.4 V was obtained for [choline][DHP] doped with 18% H$_3$PO$_4$ and a 0.78 V OCV was obtained for [choline][DHP] doped with 4% HNTf$_2$.

Experimental studies allow us to know how an electrolyte membrane works in a fuel cell system. However, it is important to have a better understanding of structures on the molecular scale, as well as larger scale morphological structures and chemical functionalities of electrolyte membranes. Molecular simulation techniques, such as molecular orbital and molecular dynamic (MD) calculations are useful tools to investigate local microstructure and micro-dynamics of molecular systems. These methods provide information that cannot be obtained by experimental investigations. There are several studies in literature about the characterisation of PFSA membranes and derivatives using computational methods [152, 153]. Dissipative particle dynamics (DPD) simulations were carried out by Wu and co-workers to better understand how molecular weight affects the hydrated morphology of the short-side-chain perfluorosulphonic acid fuel cell membranes. They found that there is a strong influence of molecular weight on both the shape and size of water-rich ionic aggregates formed as a function of water content, particularly for high equivalent weights [154]. The effects of hydration level and temperature on the nanostructure of an atomistic model of a Nafion membrane and the vehicular transport of hydronium ions and water molecules were studied by Venkatnathan et al. through classical molecular dynamic simulations. Structural and dynamical parameters such as density, radical distribution functions, coordination numbers, mean square derivations and diffusion coefficients showed that hydronium ions themselves contribute in modifying the interfacial structure of sulfonated pendants in the membrane. At low hydration levels, short hydrogen bonded linkages made of water molecules and hydronium ions alone give a more constrained structure among the said sulfonated chains. The calculated diffusion coefficient for water was in accordance with experimental data. The diffusion coefficient for the hydronium ions was 6-10 times smaller than that for water. Temperature had a significant effect on the absolute value of the diffusion coefficients for both water and hydronium ions [155]. In the work of Kumar and Paddison [156] chemical degradation of the side-chain of perfluorosulfonic acid membranes by hydroxyl radical was examined, concluding that the C-S bond was the weakest bond in the said chain of PFSA monomer. However, its cleavage was kinetically hindered.

Proton transport pathways in a triethylammonium triflate ionic liquid-doped Nafion membrane were evaluated using quantum chemistry calculations. The IL-doped membrane matrix contains triflic acid, triflate anions, triethylamine and triethylammonium cations. The quantum chemistry calculations predict that anions are responsible for proton-exchange between cations and neutral molecules of a tertiary amine. The results obtained with computational methods supported the experimental choice of IL to provide PFSA membranes with high conductivities [157].

Table 3. Comparison of PEMFC electrolytes

	Membrane	Conductivity	Thermal and mechanical properties	Fuel cell performance	Operation conditions	References
	PFSI (Nafion)	7.4×10^{-2} S cm^{-1} at 95 °C (N115)	Excellent chemical and electrochemical stability. Requires gases humidification	≈1000 mA cm^{-2} at 0.5 V. Membrane started to dry up at temperatures of approximately 50 °C, resulting in a poor performance	80 °C. Humidified gases	151 158 159
	Nafion/ SO$_3$H functionalised laponite	3×10^{-2} S cm^{-1} at 25 °C	Inorganic particles contribute to a dehydration delay of the membrane	720 mA cm^{-2} corresponding with an increase of power density of 20% in comparison with Nafion	80 °C. 4 bar. Humidified gases	53
Perfluorosulphonic acid	Nafion/15 wt% silica	1.11×10^{-1} S cm^{-1} at 25 °C	Silica improves the water retention at high temperatures	30% increase in cell performance (≈3000 mA cm^{-2} at 0.4 V)	Without humidification. 60 °C. Ambient pressure	151
	Recast Nafion/ZrP	≈1.2×10^{-1} S cm^{-1} at 100 °C	ZrP enhances water retention and improves proton conduction	1500 mA cm^{-2} at 0.45 V	130 °C. 3 bar. Humidified gases	160
	Silicon oxide/Nafion	None reported	Water uptake increases. Robust membranes	Current density 4 times higher than that of N115	130 °C. 3 atm. Humidified gases	161
Partially fluorinated	PFA/PTFE	1.7×10^{-1} S cm^{-1} at 60 °C	Tg at approximately 105 °C. Thickness between 15-30 μm	630 mW cm^{-2}	60 °C. Humidified gases	9
	Nafion film reinforced with PPSU	5.9×10^{-2} S cm^{-1} at 80 °C	Excellent water swelling and mechanical performance	507 mW cm^{-2}	80 °C. Humidified gases	162

Category	Material	Conductivity	Comments	Performance	Conditions	Ref
	High-purity Nafion nanofibres (99.9 wt) with PEO	1.5 S cm^{-1} at 30 °C	400 nm fibre diameter. Sensitive toward changing humidity	None reported	90% RH	163
	Cross-linkable sulphonated poly(ether sulphone)	1.2×10^{-1} S cm^{-1} at room temperature	Good insolubility in boiling water. Thermally stable for PEMFC applications	1500 mA cm^{-2} at 0.6 V	70 °C. Humidified gases	19
	SPEEK/ZrP	3.0×10^{-2}–9.0×10^{-2} S cm^{-1} at 100 °C	Satisfactory mechanical properties, specifically tear resistance and flexibility	1000 mA cm^{-2}	Humidified gases	20
Non-fluorinated	SPEEK/powdered heteropolycompounds	1.0×10^{-1} S cm^{-1} above 100 °C	Increasing the degree of sulphonation, the polymer increases its hydrophilicity, facilitating proton transport	None reported	None reported	21
	SPEEK/amino-functionalised silica	1.0×10^{-1} S cm^{-1} at 120 °C	Silica reduces swelling and improve water retention	246 mW cm^{-2}	120 °C. Humidified gases	30
	SPEEK/PSf-BTraz	4.9×10^{-2} S cm^{-1} at 25 °C	Proton conductivity increase with temperature. Higher proton conductivity and lower methanol crossover compared to SPEEK.	Maximum power density 2 times higher than that of Nafion 115	DMFC. 80 °C. 1M	31
Acid-base	PBI/H$_3$PO$_4$	2.5×10^{-2} - 6.8×10^{-2} at 200 °C (depending on the doping level)	Compromise between the conductivity and mechanical strength. Acid can leach from the membrane	1000 mW cm^{-2}	200 °C. No humidification	39
	PBI/SPSF/H$_3$PO$_4$	2×10^{-2} – 1×10^{-1} S cm^{-1}	SPSF improves mechanical strength at high temperatures	650 mA cm^{-2} at 0.5 V	190 °C. No humidification	44

	Material	Conductivity	Notes	Performance	Conditions	Ref
Polymer/ionic liquid blends	[MIm][Tf$_2$N]/PBI	1.86 x 10^{-3} S cm^{-1} at 190 °C	Outperforms Nafion 117 at temperatures above 95 °C. Enough thermal stability to operate from 150-190 °C	39 mW cm^{-2}	150 °C. No humidification	9
	Nafion 112/[DTA][CL]	None reported	Higher thermal stability and lower water loss for modified samples. Increase in the electrical resistance. The methanol diffusion was reduced two-fold	None reported	None reported	83
	Nafion 112/[HSO$_3$-BBIm][TfO]	None reported	[HSO$_3$-BBIm][TfO] is thermally stable up to 300 °C	217 mA cm^{-2}	25 °C. No humidification	84
	P(VDF-co-HFP)/ s-DFBPHFDP/[EMIm](FH)$_{2.3}$F	3.47 x 10^{-2} S cm^{-1} at 130 °C	Enough thermal stability to operate at temperatures above 100 °C	20.2 mW cm^{-2} at 60.1 mA cm^{-2}	120 °C. No humidification	91
	SPEEK/[EMIm][DEP]	3.1 x 10^{-3} S cm^{-1} at 145 °C	Thermal stability exceeds that of the pristine material (up to 250 °C). Membranes require better mechanical stability. Composite membranes have oxidation stability two-fold that of pristine SPEEK	203 mW cm^{-2}	145 °C. No humidification	97
	SPI/[dema][TfO]	≈1.0 x 10^{-3} S cm^{-1} at 120 °C (50wt% [dema][TfO]	Unstable three-phase boundary in the catalyst layer formed by leaked [dema][TfO]	400 mA cm^{-2} and 100 mW cm^{-2}	120 °C. No humidification	102
Polymerisable ILs	Poly(1-[2-(acryloyloxy)ethyl]-3-ethylimidazolium TF$_2$N)/ crosslinker containing an ionic liquid monomer	≈1.3 x 10^{-4} S cm^{-1} at 50 °C	When 200 mol% EMIBF$_4$ was added, the conductivity increased up to that of the monomer (3.6E-3 S cm^{-1} at 50 °C). Thermal stability above 400 °C	None reported	None reported	80

Material	Conductivity	Comments	Performance	Conditions	Ref
Poly([HSO$_3$-BVIm][TfO])	None reported	High thermal stability (up to 300 °C). The mechanical strength need to be improved	154 mA cm^{-2} and 33.1 mW cm^{-2}	25 °C. No humidification	84
poly(vinylimidazolium-co-3-sulphopropyl acrylate); poly(vinylimidazolium-co-vinylsulphonate)	Poly(vinylimidazolium-co-3-sulphopropyl acrylate) 1.2 x 10^{-5} S cm^{-1} at 50 °C, poly(vinylimidazolium-co-vinylsulphonate) < 1.0 x 10^{-9} S cm^{-1} at 50 °C	Flexible spacer is effective for improving ionic conductivity	None reported	None reported	127
P(ACxEImTF$_2$N)(x=3,6,12); P(EImVS)	1.0 x 10^{-4} S cm^{-1} at room temperature	The freedom of the imidazolium cation affects the ionic conductivity. Polycation ILs with flexible long spacers exhibit the same conductivity as polyanions without the spacer.	None reported	None reported	130
P(EITH$_6$A)	1.1 x 10^{-4} S cm^{-1} at 30 °C	To enhance mechanical properties, 0.5 mol% of E$_x$A was added, obtaining flexible films	None reported	None reported	128
OIPCs					
[N$_{1,1,1,2OH}$][DHP]; [C$_4$mim][DHP]	1.0 x 10-6 -1.0 x 10^{-3} S cm^{-1} for [N$_{1,1,1,2OH}$][DHP]. 1.0 x 10^{-4} S cm^{-1} for [C$_4$mim][DHP] in the plastic crystalline phase	DHP salt is thermally stable up to 200 °C	None reported	None reported	145
Cellulose acetate support with [Choline][DHP] and various acids	None reported	High thermal stability (up to 200 °C) except for 12% TfOH + [choline][DHP]	Zero OCV in their dry states. When the electrolytes contained 50 wt% water, an OCV of 0.4 V for 18% H$_3$PO$_4$ and of 0.78 V OCV for 4% HNTf$_2$ containing [Choline][DHP] was obtained	80 °C	146

5. CONCLUSIONS

The continued progress in proton exchange membrane research for fuel cells demonstrates the extensive interest in this technology. Perfluorosulphonic acid membranes have been the most used electrolytes for low temperature devices. However, to improve the efficiency of this technology, better performing membranes are required. To reduce the high cost and fuel crossover, perfluorosulphonic acid was replaced in part or completely by other polymer bases, such as aromatic or hydrocarbon polymers. However, these membranes have a limited durability. Basic membranes doped with acidic components were studied, demonstrating high ionic conductivity. Nevertheless, the loss of the acid component during operation limits the application of these membranes. Further progress is needed in this field, particularly during the search for novel polymeric materials with high performance that meet the requirements of fuel cells electrolytes.

The attractive properties of ionic liquids encourage their application in these electrochemical devices. Their high proton conductivity, even under anhydrous conditions, enables their use at higher temperatures than conventional membranes. To synthesise membranes with good physical properties, numerous authors have studied the performance of mixtures containing ionic liquids and polymers. However, the most direct and innovative technique used to implement ionic liquids in fuel cells is the use of polymerisable ionic liquids. Organic ionic plastic crystals are receiving significant attention because their solid transitions are beneficial for fuel cell-based applications.

The right ion pair molecular design of ionic liquids and organic ionic plastic crystals could provide a membrane electrolyte network with high performance in a fuel cell replacing conventional membranes and promoting this technology as an attractive an efficient future energy source.

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FIGURE CAPTIONS

Figure 1. Number of publications describing fuel cells (Database: Scopus. Search Keywords: Fuel Cells and Fuel Cell)

Figure 2. Schematic of a PEMFC

Figure 3. Chemical structure of Nafion

Figure 4. Chemical structure of PBI

Figure 5. Difference between ionic liquids and ionic solutions. (S): solvent, (+): cation, (-): anion

Figure 6. Cations and anions typically used to form ionic liquids

Figure 7. Poly(ionic liquids)

Figure 8. Chemical structure of [HSO$_3$-BVIm][TfO]

Figure 9. Structures of [N$_{1,1,1,2OH}$][DHP] and [C$_4$mim][DHP]
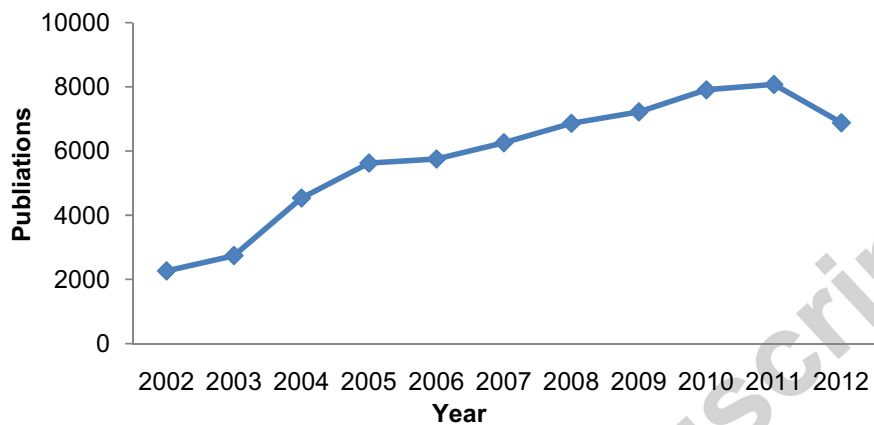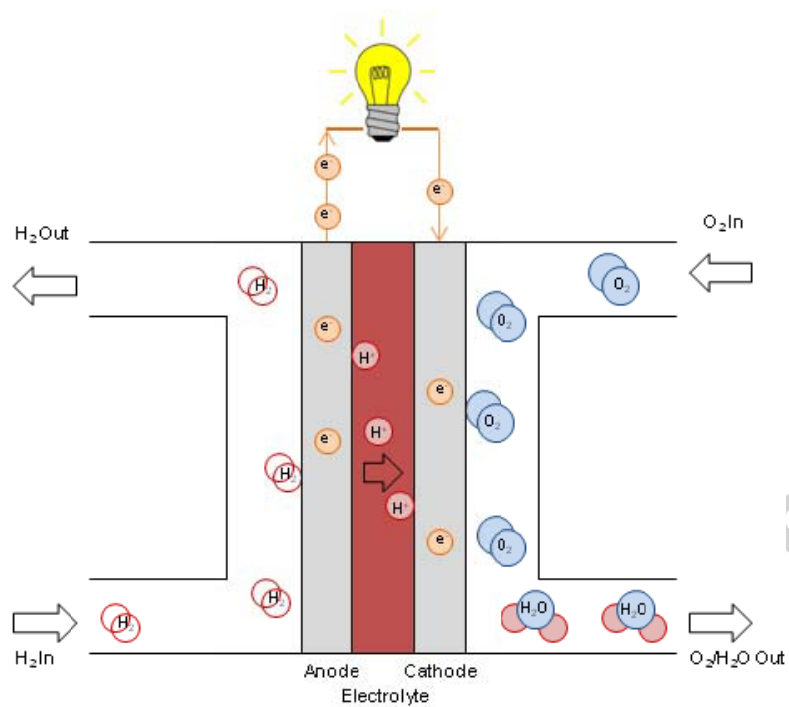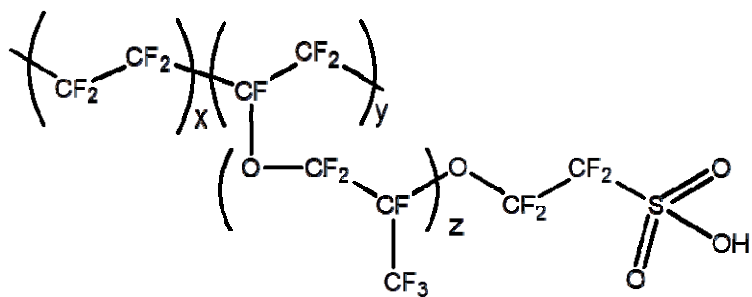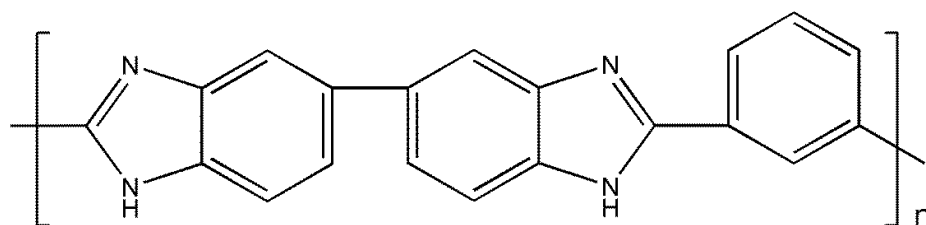
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FIGURES

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

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FIGURE 5

FIGURE 6

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FIGURE 7

Poly(zwitterion) Poly(cation) Poly(anion)

Copolymer Polycomplex Network
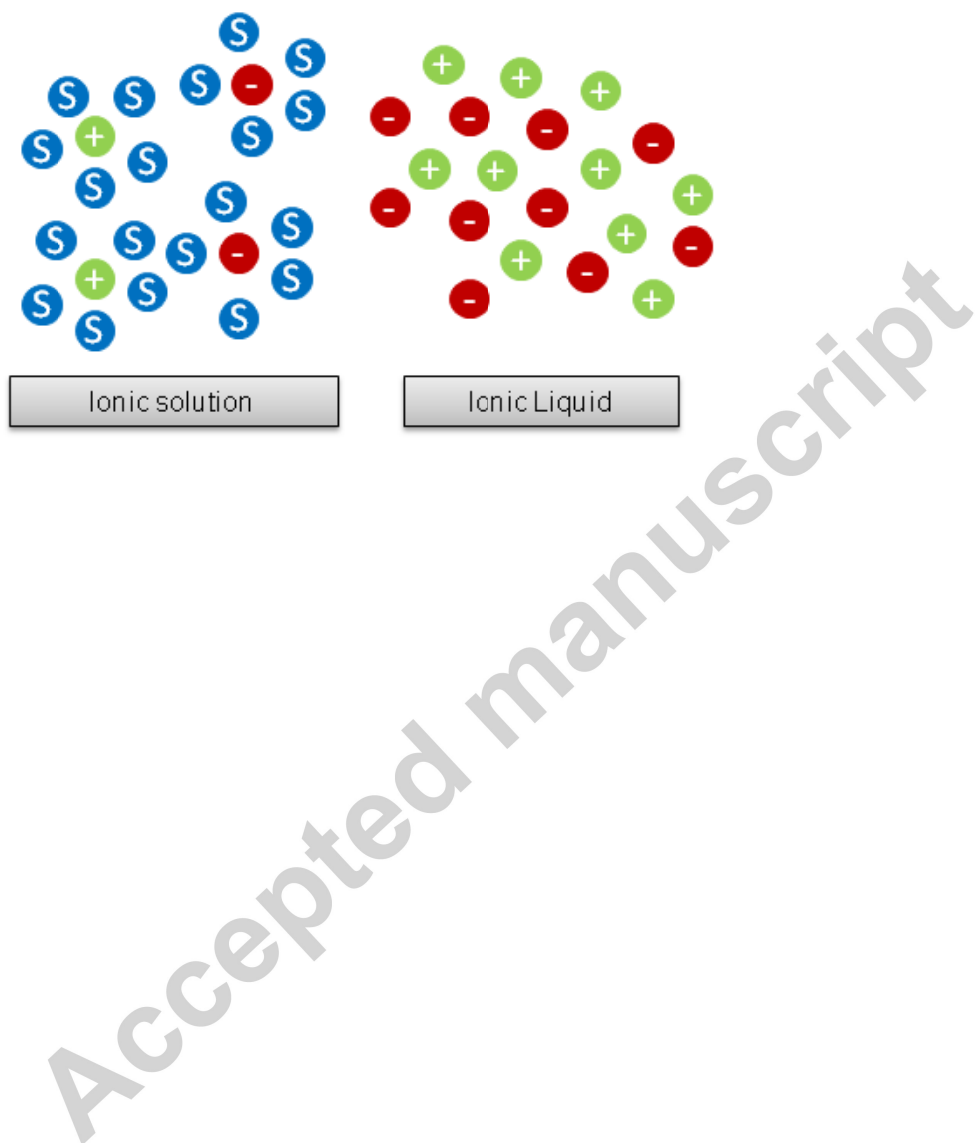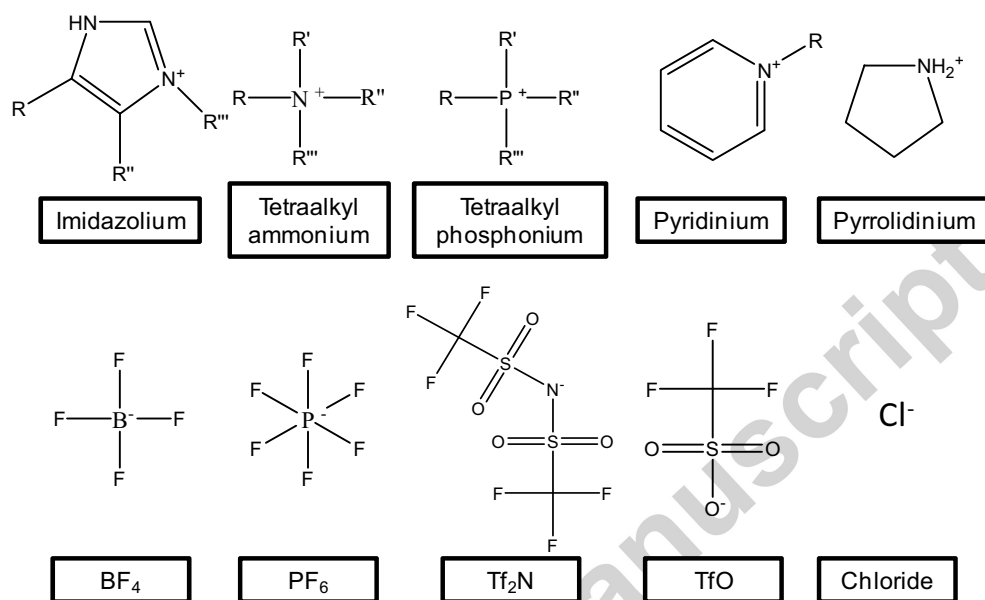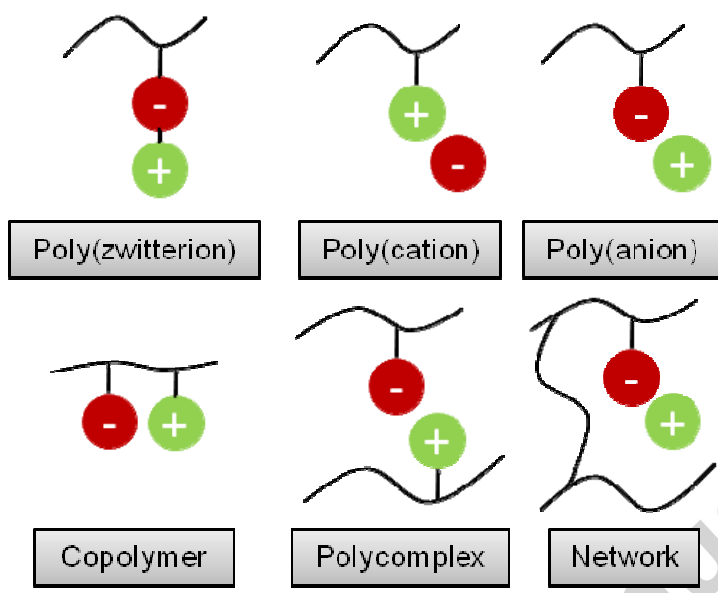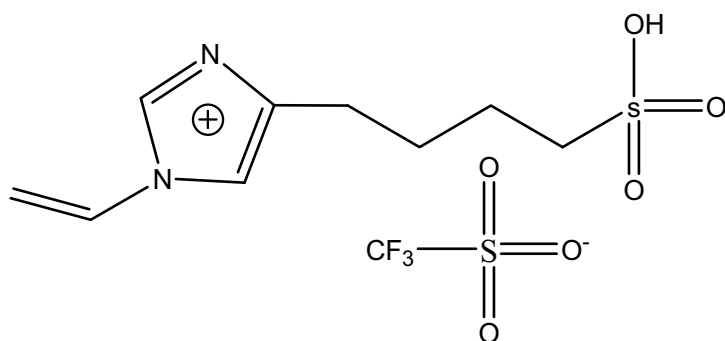
FIGURE 8

FIGURE 9
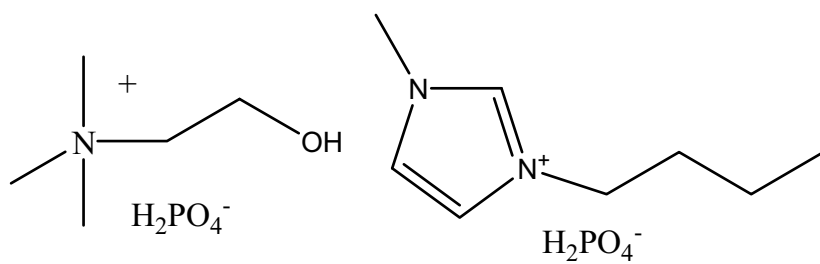
Highlights:

- Advances in ionic liquids membrane electrolytes for fuel cells are reviewed
- Polymerised ionic liquids are promising proton exchange membranes
- Right ion pair molecular design of ionic liquids must be addressed
- An overview of different electrolytes is discussed