Short communication

Proton-conducting membranes based on protic ionic liquids

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Abstract

New classes of proton-conducting membranes formed by incorporating Brönsted acid–base ionic liquids in a poly(vinyldenefluoride-*co*-hexafluoropropylene) PVdF polymer matrix, are here reported and discussed. We show that these membranes are characterized by high, thermally stable proton conductivity. However, this favourable property is in part contrasted by the release of the ionic liquid component, which may affect the long-term stability of the membranes. Various strategies are underway in our laboratory to solve this issue, and in this work we describe one of them, based on the dispersion of selected ceramic fillers in the polymer matrix. We show that this approach, while successful in enhancing the conductivity of the membranes, is not much effective in preventing the release of the ionic liquid component and thus, that other roads have to be explored to reach a satisfactory improvement of the integrity of the membrane.
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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are promising power sources for electric vehicle applications. The practical use of these electrochemical devices, however, is still prevented by a series of drawbacks, mainly associated to the polymer electrolyte. Common PEMFC prototypes are based on perfluorinated ionomeric, Nafion-type membranes. The choice is motivated by the good chemical stability and mechanical strength of these membranes. Also the ionic conductivity is relatively high, although limited to moderate temperatures. This may be a serious issue since operation temperatures higher than 100 °C are desirable for several reasons, such as to increase the kinetics for fuel oxidation and to reduce catalyst poisoning phenomena.
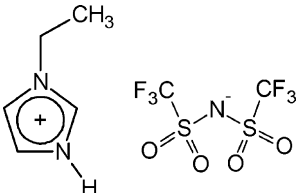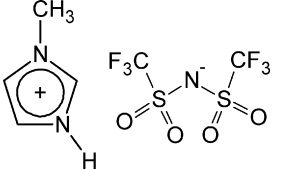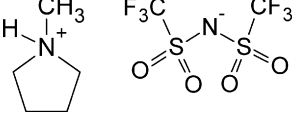
Several approaches have been pursued to obtain membranes capable to keep the conductivity at high temperature. These include: (i) the modification of conventional membranes by adding ceramic components [1,2], (ii) the development of new types of membranes using proton-conducting ionomeric polymers different then Nafion [3] and (iii) the use of inert polymer matrices impregnated with an acidic component as the proton source [4,5].

Along line (iii) a systematic work has been carried out in our laboratory for the development of ionic liquid, IL-based membranes [6]. ILs, molten salts at temperatures below 100 °C, are achieving wide interest in electrochemistry. While several papers dealing with application in lithium batteries have been reported [7–9], limited work has been so far devoted to the use of ILs as electrolyte components in PEMFCs. This is somewhat surprising, since ILs have intrinsic properties, such as high thermal stability, which can be of great relevance for the progress of the fuel cell technology. This may be particularly true for selected types of ILs, such as the Brönsted acid–base molten salts derived from the combination of organic amines and a strong acid which offers intrinsic proton conductivity [10,11]. Indeed, we have succeeded to incorporate these protic ILs in a poly(vinyldenefluoride-*co*-hexafluoropropylene) PVdF polymer matrix and shown that this membrane acts as a high thermally stable proton-conducting membrane [12]. However, the long-term operation of these membranes may be affected by a progressive release of the IL component. In the attempt of solving this issue, in this work we have considered composite membranes formed by dispersing selected ceramic fillers in the polymer matrix, with the idea that the ceramic component could enhance the retention of the IL component within the matrix.

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Table 1
Series of the ILs used for the preparation of the membranes developed in this work

Name	Structure
N-Ethylimidazolium TFSI (EImTFSI)	
N-Methylimidazolium TFSI (MImTFSI)	
1-Methylpyrrolidinium TFSI (MPyTFSI)	

2. Experimental

Two types of membranes were prepared, here classified as: (i) plain (ceramic-free) and (ii) composite (with addition of Al$_2$O$_3$ or SiO$_2$ ceramic fillers).

Poly(vinylidenfluoride) (PVdF-*co*-HFP, Kynar Flex 2801, 100,000 MW, 11–12% hexafluoropropylene copolymer, Atofina) powder was used as the polymer matrix, and 4-methyl-2-pentanone (MP, Aldrich) as the casting solvent. The ionic liquids *N*-ethylimidazolium bis(trifluoromethanesulfonyl) imide (EImTFSI), *N*-methylimidazolium bis(trifluoromethane-sulfonyl)imide (MImTFSI), and 1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (MPyTFSI) were synthesized in our laboratory following the procedure described in previous works [12]. Their structure is reported in Table 1.

The ceramic additives are silica (Silica fumed, 0,011 micron, Aldrich) and alumina (Aluminum oxide, neutral, 150 mesh, Aldrich). The preparation of the membranes is carried out by dissolving the IL in MP, in argon atmosphere. The solution is mixed with PVdF, or with a mixture of PVdF and ceramic powder (1:1 weight ratio). The mixture is stirred to obtain a homogeneous solution, which is cast into a pre-heated (70–75 °C) Petri dish. The system is subjected to cooling—heating cycles, between room temperature and 75 °C, to obtain a complete gelification. The solvent was removed by under-vacuum evaporation to obtain a self-standing membrane. Fig. 1 illustrates the appearance of a typical example of a composite, type (ii) membrane (B) in comparison with that of a corresponding, ceramic-free, type (i) membrane (A). According to results previously obtained in our laboratory [12], the 6:4 IL/PVdF weight ratio was chosen for the type (i) plain membranes. The 60% IL content was kept in the type (ii) membranes also, adjusting the PVdF/ceramic composition. The mean thickness value of the various samples was 200 μm.

The thermogravimetrical analysis (TGA) of the membranes was carried out from room temperature up to 500 °C, at 5 °C min^{-1} (TGA/SDTA 851 Mettler-Toledo instrument).

The ionic conductivity of the membranes was determined by means of complex impedance spectroscopy (CH Instruments CHI 660A) scanning the frequency from 100 kHz to 100 Hz, with an amplitude of 0.01 V. The measurements were performed in argon atmosphere, on a Teflon cell in which the membrane was sandwiched between two platinum electrodes.

The Fenton test was carried out according to the following protocol. The membrane samples were dried in oven until they reached a constant weight. They were then immersed in a Fenton solution (3% H$_2$O$_2$, 2 ppm Fe^{2+} aqueous solution) at 80 °C for 3 h. When the test was stopped, the membranes were soaked in cold distilled water at room temperature to quench the reaction, and dried again until constant weight was reached. The stability of the samples is indicatively measured by the weight loss they suffered, expressed by the following relation:

$$\text{w.l.}(\%) = \frac{P_i - P_f}{P_i} \times 100 \tag{1}$$

3. Results and discussion

The acronyms and compositions of the different types of IL-based membranes prepared in this work are listed in Table 2.
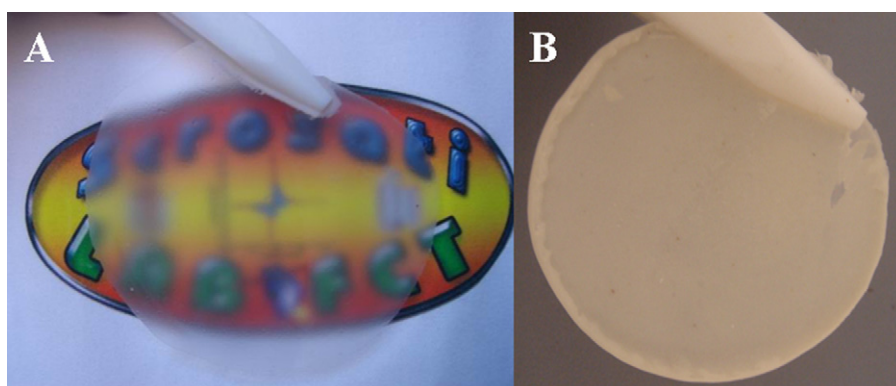

Fig. 1. Pictures of MImTFSI–PVdF (A) and MPyTFSI–PVdF–Al$_2$O$_3$ (B) membrane samples.

Table 2
Acronyms and composition of the membranes developed in this work

Membrane type	Sample name	Sample composition (wt%)		
		PVdF (%)	IL (type and composition)	Ceramic (type and composition)
Type (i)	EImTFSI60	40	EImTFSI 60%	–
	MImTFSI60	40	MImTFSI 60%	–
	MPyTFSI60	40	MPyTFSI 60%	–
Type (ii)	MPyTFSI60a	20	MPyTFSI 60%	Al_2O_3 20%
	MPyTFSI60s	20	MPyTFSI 60%	SiO_2 20%

In all the cases the IL acts as the conducting component, while the polymer acts as the plastic component [6]. It is expected that the dispersion of the ceramic filler may reflect in an improvement of the membrane properties, especially in terms of retention of the IL component.

Fig. 2 shows the TGA response of the two types of membranes here considered. It can be noted that the membranes lose less than 10% in weight up to 300 °C, confirming that the IL component indeed confers a high thermal stability, far beyond the range of interest for application in PEMFCs. The addition of the ceramic slightly decreases the decomposition temperature, see the response of the type (ii) composite membrane for the selected case of the Al_2O_3-added MPyTFSI 60%-PVdF sample. The figure shows that the residual weight is about 20% larger than that of the corresponding type (i) membrane, this matching with the amount of the added alumina.

The thermal stability is reflected in the conductivity trends of the membranes. All the samples show no decay in conductivity even at temperatures as high as 140 °C, reaching values of 10^{-2} S cm^{-1} in the case of the EImTFSI60 sample (data not shown). Some differences can be observed between the conductivity plots of type (ii) composite membranes and those of type (i) plain membranes, shown as Arrhenius plots in Fig. 3. The IL here considered, MPyTFSI has a peculiar solid–solid physical transition around 50 °C, and it shows a reasonably high conductivity only above this transition temperature [12]. The MPyTFSI-based type (i) membrane follows the same trend. The addition of the ceramics to these systems appears to considerably improve the conductivity, such as to make possible its exper-
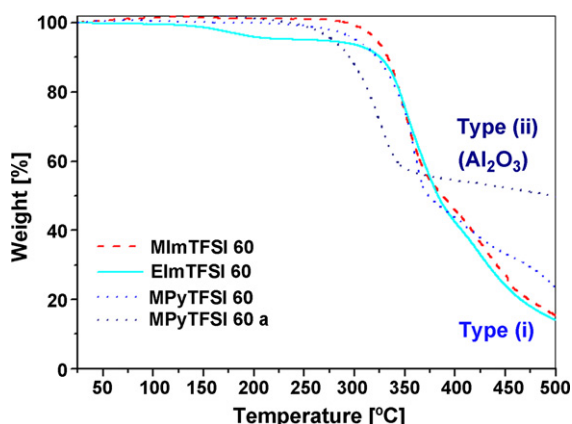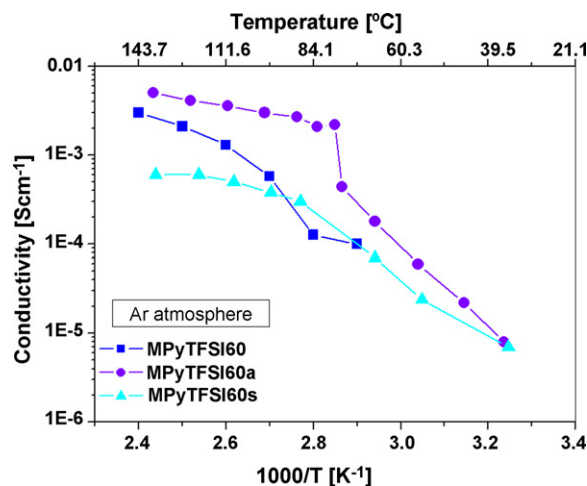

Fig. 3. Conductivity Arrhenius plots of the MPyTFSI-PVdF membranes.

imental determination even at temperatures as low as 35 °C. Probably, the presence of the additives favours the transition of the MPyTFSI to the plastic phase, this finally enhancing its conducting properties.

To be noticed that the conductivity of these IL-added membranes, either plain or composite, is very stable, as demonstrated in Fig. 4 which shows the conductivity of a representative sample, i.e. the MPyTFSI60 membrane, which remains almost unchanged for several days at 130 °C. It is worth to point out that all the measurements are carried out in argon atmosphere,

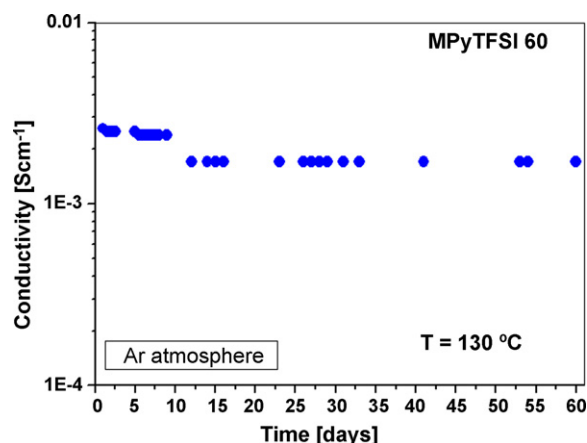Fig. 2. TGA thermograms of the protic IL-PVdF membranes developed in this work.

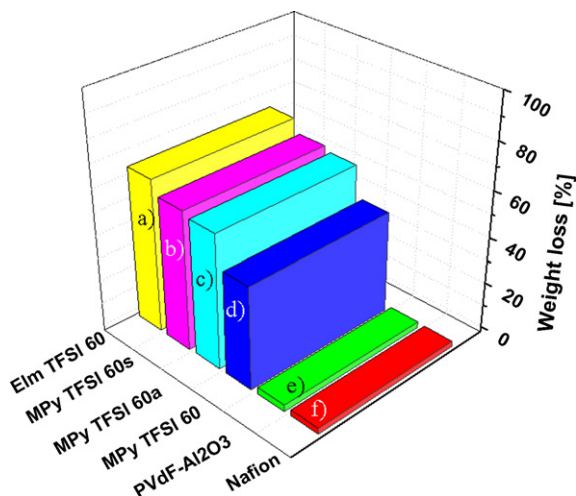Fig. 4. Time-stability of the ionic conductivity of the MPyTFSI60 membrane at 130 °C.

Fig. 5. Results of the Fenton test carried out on type (i) plain and type (ii) composite membranes. Also the test results for Nafion 117 and PVdF-Al$_2$O$_3$ (no IL-added) membranes are reported for comparison purposes.

Fig. 6. Results of the water-stability test carried out in type (i) plain and type (ii) composite membranes.

this demonstrating the independence of the conductivity from ambient humidity.

Fig. 5 shows the weight loss of a series of membranes after treatment with a Fenton solution, formed by a 3% H$_2$O$_2$, 2 ppm Fe^{2+} aqueous solution. The membranes tested included: (a) EImTFSI-based, type (i) membrane; (b) SiO$_2$-added MPyTFSI, type (ii) composite membrane; (c) Al$_2$O$_3$-added MPyTFSI, type (ii) composite membrane; (d) MPyTFSI-based, type (i) membrane; (e) simple PVdF–Al$_2$O$_3$ (no IL-added) membrane and (f) conventional Nafion 117 membrane. A minor weight loss is observed for Nafion, this confirming its expected high chemical stability. On the contrary, the membranes incorporating ILs, either plain or composite, are affected by a considerable weight loss. This cannot be ascribed to a decomposition of the polymer matrix since the plain PVdF–Al$_2$O$_3$ (no IL-added) membrane shows negligible weight loss, see case (e). Also a decomposition of the IL can be excluded since these salts have an established, high chemical stability.

Thus, the weight loss determined for the IL-based membranes can be reasonably ascribed to the extraction of the protic IL component by the aqueous phase. The model was confirmed by determining the weight loss of various membrane samples after immersion in plain water at 80 °C for 3 h. Fig. 6 shows the results in the case of: (a) MImTFSI-based, type (i) membrane; (b) MPyTFSI-based, type (i) membrane; (c) Al$_2$O$_3$-added MPyTFSI, type (ii) composite membrane and (d) SiO$_2$-added MPyTFSI, type (ii) composite membrane. The results show that in all types of membranes the IL is largely extracted from the polymer matrix. The difference in weight loss observed between the MImTFSI60 and the MPyTFSI60 samples accounts for this interpretation: MPy is a stronger base than MIm, this resulting in an IL more stable and less affected by hydrogen bonding with water. The weight loss of the alumina-added membrane is slightly lower than that of the silica-added one, in line with the higher absorbent properties shown by alumina towards organic solutions due to dipolar interactions or hydrogen bonding. However, for both the ceramic-added, type (ii) membranes,
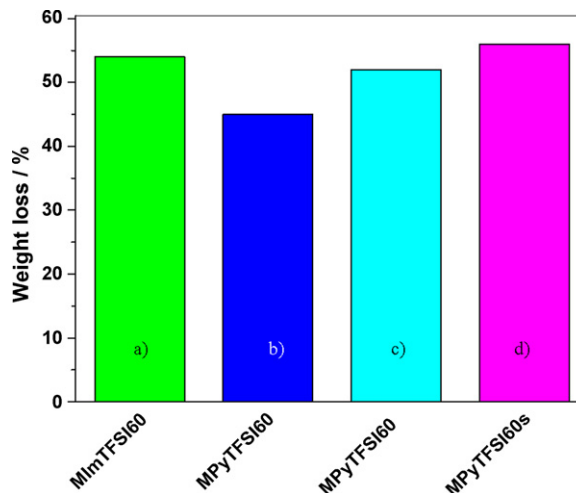
the weight loss is even larger than that experienced by the type (i) plain membranes. This is probably due to the water interaction with the additives, which favours the IL movement from the absorbing sites, finally promoting its release.

We can conclude that the addition of the ceramic filler, while having a positive role for the conductivity properties of the membranes, is not effective in retaining the IL into the polymer matrix. This problem is actually under study in our laboratory, where we are evaluating new, possible strategies to solve it.

4. Conclusions

The above described results demonstrate that the IL-based membranes, while apparently stable in terms of thermal and transport tests, loose their integrity under drastic conditions, such as treatment with the Fenton solution, or even when in contact with a water phase, i.e. under conditions which mimic the operating conditions in a fuel cell. We have shown that apparently the addition of the ceramic filler is not effective in preventing the release of the IL component and thus, that other strategies must be considered to improve the integrity of the membranes. We are presently exploring various alternatives approaches. A promising one is the use of polymer matrices which may anchor the IL component, thus preventing its release by entrapping it into the membrane. Crosslinked matrices appear as a good choice since they are expected to have an improved chemical stability. We plan to test this concept and the results will be reported in a following paper.

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