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ORIGINAL PAPER

Aprotic ionic liquids as electrolyte components in protonic membranes

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Abstract In this paper we describe the preparation and the properties of a series of aprotic ionic liquid-based, proton-conducting membranes. The ionic liquids (ILs) 1,2-dimethyl-3-*n*-propylimidazolium bis(trifluoromethanesulfonyl)imide and the 3-methyl-1-*n*-propylpyridinium bis(trifluoromethanesulfonyl)imide are used as the casting solvents of PVdF gel-type membranes; the proton conductivity is achieved by the addition of a superacid component, namely, trifluoromethanesulfonic acid (HTf) or N,N-bis(trifluoromethanesulfonyl)imide (HTFSI). The polymer electrolytes showed good thermal and electrochemical properties in the temperature range of interest for PEMFC applications. The strong coordination between the ILs and the HTFSI, which have the same anion, improves the thermal stability of this kind of membrane, but lowers the chemical properties and the conductivity, due to an increase in viscosity. HTf-added samples have an ionic conductivity of 2×10^{-2} S cm^{-1} at 100 °C, showing the best overall properties and making these membranes of interest applications in fuel cells.

Keywords Ionic liquids · Membrane · Proton conductivity · Fuel cells

1 Introduction

Fuel cell technology has been gaining considerable interest in the development of new, eco-compatible energy sources. Up to now, the most promising devices for low temperature applications are the polymer electrolyte membrane fuel cells (PEMFCs), generally using perfluorinated, e.g. Nafion-like, membranes. The operational temperature range of this type of cell is limited to 100 °C, due to performance decay at higher temperatures [1, 2]. These decays are related to: (i) dehydration of the membrane, with the consequent reduction of ionic conductivity; (ii) loss of mechanical strength due to softening of the polymer backbone; (iii) consistent increase of fuel permeability. Actually, high temperature-operating devices would be desirable for several reasons, including reduction of catalyst poisoning by CO and improvement of the kinetics of the fuel oxidation, all leading to an enhancement of cell efficiency.

Ionic liquids (ILs) are attracting increasing interest as alternative electrolyte components for several technologies, such as batteries, solar cells, capacitors and, so far to a less extent, fuel cells [3]. The advantageous properties of ILs include high thermal stability, very low volatility, non-flammability and a wide temperature range of the liquid phase existence [4]. We already succeeded in preparing novel gel-type membranes composed of an IL and a poly(vinylidenfluoride)-co-hexafluoropropylene (PVdF) matrix [5]. In these membranes proton conduction was achieved by the addition of a superacid, i.e. trifluoromethanesulfonic acid, HTf. In this work, we continue study of this class of membrane, extending the analysis to different ILs and acids. We prepared samples varying the composition of the membranes, in order to establish the influence of the IL cation and of the acid on the thermal, electrochemical and chemical properties of these electrolyte systems.

2 Experimental

The ILs reported here are 1,2-dimethyl-3-*n*-propylimidazolium bis(trifluoromethanesulfonyl)imide (DMPITFSI) and

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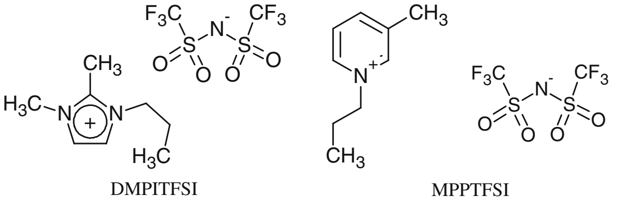

Fig. 1 Structures of the ILs used in the preparation of the membranes studied in this work

3-methyl-1-*n*-propylpyridinium bis(trifluoromethanesulfonyl)imide (MPPTFSI), provided by Covalent Associates, Inc. Their structures are given in Fig. 1. The poly(vinylidenfluoride) Kynar Flex 2801, 100,000 Mw, 11–12% hexafluoropropylene copolymer (PVdF) was purchased from Atofina; the trifluoromethanesulfonic acid (HTf) was purchased from Aldrich; and the bis(trifluoromethanesulfonyl)imide (HTFSI) was purchased from Morita Chemical Industries, Co. Ltd. All the reagents were used as received.

The IL-based membranes were prepared accordingly to a procedure established in our laboratory [5]. The PVdF powder and the acid were dissolved in the IL at room temperature. After mixing to homogeneity, the mixture was cast into a Teflon block, heated at 130 °C, and then quenched at room temperature. This thermal treatment was repeated several times, in order to improve the consistency and mechanical resistance of the membranes. The samples reported in this work had thickness between 200 and 250 μm.

The thermal properties of the resulting samples were investigated by differential scanning calorimetry (DSC 821 Mettler Toledo) and thermogravimetric analysis (TGA/SDTA 851 Mettler Toledo). The measurements were carried out in nitrogen and in air flux, respectively. The temperature was scanned at 10 °C min^{-1}.

The ionic conductivity was evaluated by electrochemical impedance spectroscopy (Solartron 1255B FRA), scanning the frequency from 1 kHz to 100 Hz, with an amplitude of 10 mV. The samples were sandwiched between two platinum electrodes in a Teflon-bodied cell and were kept under a water saturated atmosphere during the measurements.

The chemical stability of the membranes was estimated according to a protocol established for the evaluation of the feasibility of polymer membranes for application in fuel cells, namely the so-called Fenton test [6, 7]. The samples were dried in an oven at 70 °C until they reached a constant weight. Then they were immersed in the Fenton solution (3% H_2O_2, 2 ppm Fe^{2+} aqueous solution) and kept at 80 °C for 3 h. The test and the associated reaction were terminated by soaking the samples in cold distilled water and by drying them again until constant weight was reached. The weight loss was obtained by the following relation:

$$w.l.\% = \frac{P_i - P_f}{P_i} \cdot 100 \tag{1}$$

The result was taken as an indicative measure of the chemical stability of the membranes.

3 Results and discussion

Previous work [5], investigating the effect of the amount of acid used, established 3 wt.% acid content as the optimal composition to obtain the best-performing membranes. Therefore, the composition IL: PVdF: acid was 77: 20: 3 in all the samples prepared in this work, where only the IL and the acid types were varied.

HTf and HTFSI were chosen as the acidic proton sources because of their affinity for the IL anion, this assuring chemical compatibility of the electrolyte system components.

Figure 2 shows a typical DSC response of the membranes. The DSC test was carried within a temperature ranging from room temperature to 170 °C. All the thermograms show an endothermic peak in the region 100–110 °C, which can be assigned to the melting of the polymer, and a corresponding exothermic peak around 60 °C, which relates to the slow crystallization process. The melting points of the membranes are lower than that of the PVdF powder, which is detected at 142 °C (data not shown). This decrease may be associated with the crystallinity of the PVdF network which is expected to be lower within the membrane structure than in the pristine powder [8]. Figure 2 shows that no thermal process due to the IL component was detected. This behaviour is the same as that shown by the neat IL, whose liquid phase is stable in the whole temperature range scanned (data not shown). This result suggests that the polymer matrix just acts as an inert container.

Figure 3 shows the TGA responses. All the samples show very low weight losses up to 250 °C, mainly due to the slow removal of the acidic component. At 150 °C, i.e. at a temperature well above that afforded by Nafion-like electrolyte systems, the weight loss of the three types of membranes is only of the order of 1%.

On closer analysis, Fig. 3 may be split in two regions, below and above 150 °C. In the low temperature range, a phenomenon is clearly observed at ca. 50 °C, possibly due to the release of absorbed water. This assumption is confirmed by the fact that the process is much more evident for the membrane containing HTf, whose hygroscopicity is higher than that of HTFSI. The high-temperature side of the diagram reveals that the HTf-added sample experiences a more rapid and consistent weight loss than the HTFSI-added ones. Presumably, the higher thermal stability of the latter results from the identities of the HTFSI anions and

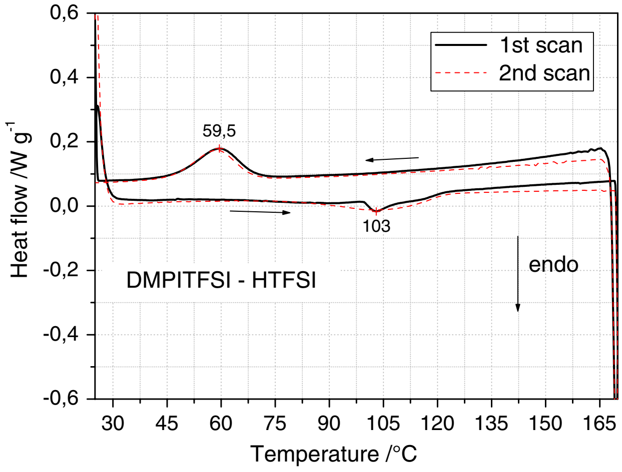

Fig. 2 DSC result of the DMPITFSI-HTFSI-PVdF sample, taken as representative example of the aprotic membranes developed in this work

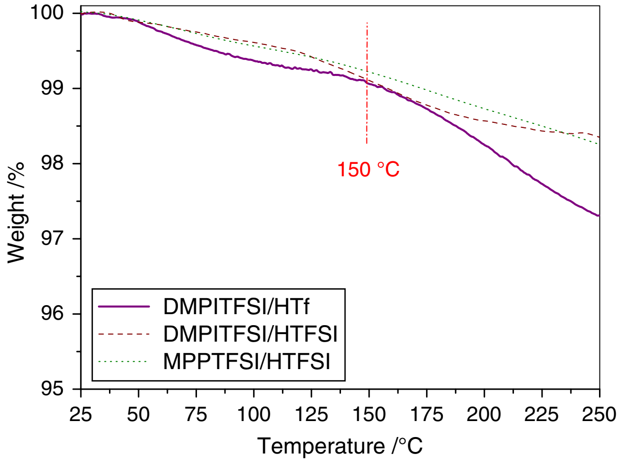

Fig. 3 TGA thermograms of the IL-PVdF membranes developed in this work

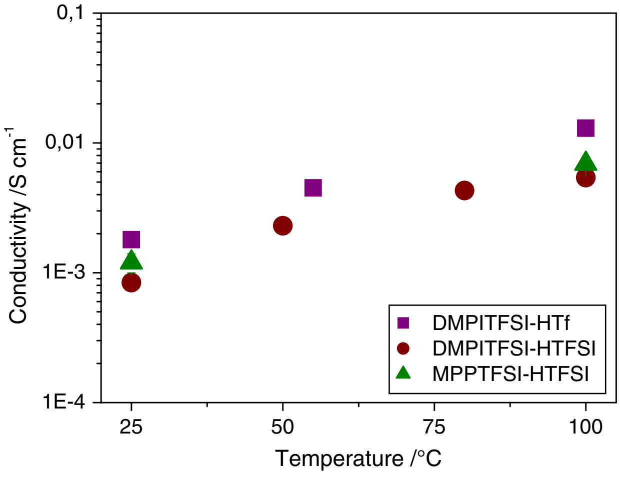

Fig. 4 Conductivity versus temperature plots of the IL-PVdF membranes developed in this work

those of the ILs used, which accounts for a strong affinity of the two components.

The thermal behaviour is reflected by the trend of the conductivity versus temperature (see Fig. 4). The conductivity data are reported as the mean values over a set of several-days measurements. The experimental error bars fall within the data point markers. At room temperature, the three membranes show similar conductivities, settling around 1×10^{-3} S cm^{-1}. On the basis of a previous study, this is an expected value for this kind of membrane containing 3 wt.% of acidic component [5]. Moreover, the conductivities of the two membranes IL-HTFSI are nearly the same, even at 100 °C. The ILs used in these two membranes have cations of similar molecular weight and shape, as well as the same anions. These are the most important structural parameters influencing the ionic transport properties [9], thus explaining the similarity in the conductivity behaviour. However, the highest conductivity at 100 °C, i.e. 2×10^{-2} S cm^{-1}, is shown by the HTf-added membrane in spite of its lower thermal stability detected by TGA (compare Fig. 3). We may attribute the lower conductivity of the HTFSI-containing samples to the increase in viscosity associated with the interactions of the TFSI anions.

The strong coordination of the HTFSI anion by the IL cations is also reflected in the chemical stability of the electrolyte membranes, investigated by the Fenton test. Results obtained for a PVdF-based membrane (conventional organic solvent, no IL) attest the stability of the polymer matrix in the oxidant, aggressive Fenton solution. The weight loss experienced by both the HTf-added and the HTFSI-added membranes (41 and 56%, respectively) cannot be associated with the decomposition of the ILs which, in fact, have a high-chemical stability. The weight loss may be ascribed to the extraction of the IL-acid mixture from the membrane via a phase inversion process already observed for similar types of gel membranes [10, 11]. The water from the solution swells the polymer network, removing the IL-based solvent, and is then released during the drying process prior to the final weighing of the sample. The removal of the acidic component from the polymer matrix is attended by the withdrawal of the IL coordinating ions. This interaction is obviously stronger in the case of the HTFSI, whose anion is the same as that of the ILs, this accounting for the difference in the weight loss suffered by the two membrane samples. However, it is worth noting that, due to the hydrophobicity of the ILs studied in this work, the ionic component is not completely released by the membranes. This suggests that more stable IL-based electrolyte systems can be achieved via a careful choice of the IL component and by its suitable combination with the polymer matrix and the acidic component.

4 Conclusions

The preparation and the properties of a series of aprotic IL-based, proton-conducting membranes was reported. The use of ILs as the casting solvents of PVdF gel-type membranes gives polymer electrolytes with good thermal and electrochemical properties in the temperature range of interest for PEMFC applications. HTFSI-containing membranes show phenomena ascribable to the strong coordination between the acid and the ILs, due to the identities of the anions. This interaction improves the thermal stability of this type of membrane, but lowers the chemical properties and the conductivity, due to an increase in viscosity. HTf-added samples, having an ionic conductivity of 2×10^{-2} S cm^{-1} at 100 °C, show the best overall properties, in spite of the lower-temperature acid removal detected by TGA. Indeed, the thermal stability of the membranes reported in this work is limited by the melting of the PVdF polymer matrix, which actually occurs at ca. 110 °C. This aspect may be improved by the suitable choice of an IL capable of interacting with PVdF, increasing its melting point. This approach is under study in our laboratories [12].

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