Electrolytes Based on Primary Ammonium Salts as Ionic Liquids for PEMFC-membranes

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Original scientific paper
Received: July 8, 2008
Accepted: November 6, 2008

Physico-chemical characterization of a series of salts prepared from primary amines was performed in order to obtain the salts as protonic ionic liquids (PILs). It was shown that the majority of these salts are thermally stable up to 400 °C, while the melting point of each salt depends on the nature of the anion and amine substitutions. The results of cyclic voltammetry experiments showed that the amines and the salts (HNR_3^+, A^-) could be oxidized only at very high potentials (> 1.9 V/SHE) which is compatible with their use in PEM fuel cells. Conductivities of salts at 130 °C are between 0.01 and 13 mS cm^{-1}. The best conductivity was observed for the salt resulting from asymmetric amines/trifluoromethanesulfonic acid association. Incorporation of these compounds within Nafion® has also been studied, particularly with respect to the compatibility of PIL/Nafion® and conductivity of these newly formed membranes.

Key words:
Fuel cells, protonic ionic liquids, Nafion$^®$, conductivity

Introduction

The proton exchange membrane fuel cell (PEMFC) is currently at the origin of one of the largest world's research and development efforts. This interest is due to the modularity of the PEMFC which allows its use in a broad range of portable applications, electric and hybrid vehicles of the future. Also, PEMFC's are integrated perfectly into the European directives promoting a sustainable energy development.

The fuel cell is an electrochemical energy generator that exploits a simple oxido-reduction reaction between H_2 and O_2 with simultaneous production of electricity, water and heat. The crucial point for the efficiency of this device lies in the control of several process parameters: i) kinetics of electrochemical reactions at the electrodes ii) maintenance of protonic conduction of the separating membrane and iii) management of produced water and heat. Operation of PEMFC at relatively high temperature (130 °C) allows optimal conditions for all process parameters. However, Nafion$^®$ membranes which are commonly used in industry do not work at optimal conditions[1,2] and therefore addition of a protonic ionic liquid (PIL) is usually considered. Apart from having a low melting point and great thermal and electrochemical stabilities, once incorporated in the membrane PIL improves protonic conduction.[3]

The components of ionic liquids shown in this work were chosen to be aliphatic ammoniums as cations, and sulfonate trifluoromethane (triflate), or the bis(trifluoromethanesulfonyl)amine (TFSI) as anions (Table 1).

Table 1 – *Anionic components used for the synthesis of salts*

Acid	Formula	Usual name of its anionic form
Trifluoromethane sulfonic acid	CF_3SO_3H	Triflate, T_f
Bis(trifluoromethane-sulfonyl)amine	$(CF_3SO_2)_2NH$	TFSI

It has generally been recommended to use less polarizable cations,[4] particularly the quarternary ammoniums which have small alkyl groups on the nitrogen atom (aprotic systems). These cations have also a wide electrochemical window (6 V) what permits their application in electrochemical devices (lithium battery system[5]). Protic ammonium cations are also admitted due to high fluidity, low glass temperature and high conductivity.[4] It has already been reported that ammonium salts ensure high thermal stability and increase the concentration of the protons carrier,[4] but it has also been shown that use of symmetrical aliphatic ammoniums did not show satisfactory results.[6]

This paper presents a study of some primary amines and the detailed study of the dependence be-

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tween their structure and physical properties. The triflate and TFSI anions show low melting points and high conductivities of the corresponding ionic liquids.[6–9] The choice of perfluorinated anions in this paper is attributed to the following: (i) by increasing the perfluoroalkyl chain, the anion's delocalisation of charge is improved, while hydrogen bonds between cation and anion become weaker. This all leads to higher conductivity and lower viscosity of ionic liquid (ii) TFSI salts are often hydrophobic and very thermally and electrochemically stable,[10] while low basicity of triflate anion contributes to the increase of chemical stability of ionic liquids.[11]

Experimental section

Synthesis

All salts were synthesized using the same experimental procedure. 53.30 mmol of acid diluted in 50 mL of ether was added in an excess to 26.65 mmol of amine in 50 mL diethyl ether. In most cases, after one hour of reflux, salts were precipitated after cooling. After recrystallization in CH_3CN/ether (1/5), the final product was dried at 60 °C under vacuum (procedure **A**). For the salts that are liquid at temperatures close to the ambient, the liquid was washed twice with 100 mL ether, the solvent removed and the salt dried at 60 °C under vacuum (procedure **B**). The purity of the compounds was checked by the elemental analysis, NMR^{1}H and electrochemical measurements, whereas anhydrous character of the salts was verified by Karl Fisher titration (H_2O less than 10 ppm). After purification, the salts were stored in a glove box. The NMR^{1}H spectra of MePrCHNH$_3^+$, T_f salt is presented in Fig. 1.

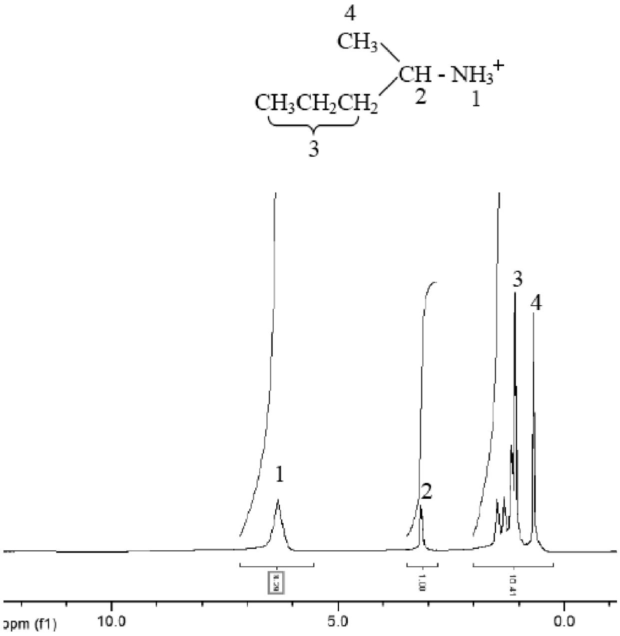


Fig. 1 – *NMR ^{1}H Spectra of MePrCHNH$_3^+$, T_f salt*

The results of elemental analysis of the prepared salts are as follows:

1. Propylammonium triflate: PrNH$_3^+$, T_f was obtained by procedure **A**, yield: 90 %, elemental analysis calculated: 22.9 % C, 4.7 % H, 6.7 % N, found: 22.5 % C, 4.8 % H, 6.5 % N.

2. Isopropylammonium triflate: iPrNH$_3^+$, T_f was obtained by procedure **A**, yield: 87 %, elemental analysis calculated: 22.9 % C, 4.7 % H, 6.7 % N, found: 21.1 % C, 4.3 % H, 6 % N.

3. Butylammonium triflate: BuNH$_3^+$, T_f was obtained by procedure **A**, yield: 93 %, elemental analysis calculated: 26.8 % C, 5.3 % H, 6.2 % N, found: 27 % C, 5.3 % H, 6.2 % N.

4. Butylammonium trifluoromethyl-sulfonimide: BuNH$_3^+$, TFSI was obtained by procedure **B**, yield: 87 %, elemental analysis calculated: 20.3 % C, 3.4 % H, 7.9 % N, found: 20.2 % C, 3.4 % H, 7.9 % N.

5. Isobutylammonium triflate: iBuNH$_3^+$, T_f was obtained by procedure **A**, yield: 89 %, elemental analysis calculated: 26.8 % C, 5.3 % H, 6.2 % N, found: 26.4 % C, 4.9 % H, 5.7 % N.

6. 1-Methylbutylammonium triflate: PrMeCHNH$_3^+$, T_f was obtained by procedure **A**, yield: 38 %, elemental analysis calculated: 30.3 % C, 5.9 % H, 5.9 % N, found: 30.1 % C, 6.1 % H, 5.7 % N.

Preparation of Nafion®

Nafion® 117 membrane (DuPont de Nemours) was used as received, cut into rectangular pieces (2x5 cm) and treated as follows: (i) boiled in 2 M nitric acid for three hours at 125 °C; (ii) washed with deionised water for three days using soxhlet and (iii) SO_3H moieties of Nafion were neutralized by the same amine of that constitutive in IL. This was achieved in 50 mL ethanol/H_2O (1/1) medium containing the amine (2 M), under inert atmosphere and during 24 hours. After washing three times by the ethanol/H_2O mixture, the pieces were dried under vacuum at 110 °C. These samples were characterized by DSC analysis in order to check the absence of water within the membrane. Finally, ILs were incorporated in the neutralized Nafion® membrane by immersion of Nafion® in the synthesized ionic liquid. In most cases four days were required to get an optimal incorporation. The membrane weight uptake was in the order of 50 %.

Thermal properties

The melting temperatures (T_m, maximum of the exothermic peak) and glass transition temperatures of the salts (T_g, middle of the slope) were determined from differential scanning calorimetry (DSC) thermograms during the heating scans from –35 to 400 °C. DSC was carried out with a TA Instruments Model 2920 under N_2 atmosphere. The samples for DSC measurements were tightly sealed by using Al pans in the glove box. The heating rates were 10 °C min^{-1}. High-temperature stabilities for the samples were measured on a Netzsch Instruments thermogravimetry/differential thermal analysis Model 409, from 30 to 550 °C at a heating rate of 10 °C min^{-1} under N_2 atmosphere with open alumina pans.

Density

Since all densitometers determine densities at temperatures lower than 40 °C, densities at high(er) temperatures were estimated by extrapolation. Because of difficulties in measuring densities of salts exhibiting melting points higher than 40 °C, a less precise method was applied that can determine only the order of magnitude of density value. Measurements were made by taking a 100 μL of the salts using a syringe and by heating the salts at a temperature higher than its melting point. The weight difference between the empty and full syringe was determined. It was supposed that the variation of density with temperature is negligible compared to the error made by the measurement.

Viscosity

Viscosities of PILs were measured by ARG2 rheometer built by TA. The ARG2 is a stress controlled rheometer equipped with an oven for performing experiments in the temperature range 20–150 °C. Viscosity of samples was measured using 25 mm diameter cylindrical plates having a gap of approximately 1000 micrometers. The volume of the sample was approximately 0.5 mL of PIL. The experiment performed is a shear stress measurement when a shear rate is applied.

Ionic conductivity

Ionic conductivities were determined by the complex impedance method using a Hewlett-Packard 4192A LF impedance analyzer in the frequency range from 5 Hz to 13 MHz. The samples were put in a dip-type glass cell with two Pt wires fixed at a constant electrode distance in the glove box and are thermally equilibrated at each temperature for at least 2 h (Yashima, BX-10) prior to the measurements. The cell constant was determined using 0.1 M KCl standard solution (Kanto) at 30 °C. For membranes, the samples were placed between two blocking steel holds in the glove box and are thermally equilibrated at each temperature for at least 2 h (Yashima, BX-10) prior measurements.

Electrochemical polarization

Cyclic voltammetry (CV) was measured in a glove box, at the ambient temperature and under dry Ar gas atmosphere. In order to investigate the overall electrochemical behavior of the salts, studies have been performed in CH_3CN (Rathburn) + 0.1 M tetrabutyl ammonium perchlorate (TBAP, Fluka), using a conventional three-electrode cell. The working electrode (WE) was a Pt wire of 0.5 mm in diameter. The counter electrode (CE) was a Pt wire, while the reference electrode (RE) was an Ag wire in 10 mM $AgNO_3$ in CH_3CN + 0.1 TBAP. Note that potentials can be converted to the NHE scale by adding 0.548 V.[12] The electrochemical control was accomplished using a Solartron electrochemical interface (Model 1287). For a reversible process, $E_{1/2}$ and ΔE_p have been determined with $E_{1/2} = \frac{1}{2}(E_{pa} + E_{pc})$ and $\Delta E_p = E_{pa} - E_{pc}$. Irreversible processes have been characterized by E_{pa} and E_{pc} values.

Pulsed field gradient spin echo NMR

NMR measurements were carried out on a 9.4 T Bruker Avance 400 NMR spectrometer equipped with a Bruker 5 mm broadband probe with a z-axis gradient and a temperature controller, allowing experiments to be performed from RT up to 170 °C (stability and accuracy ± 0.2 °C). NMR resonance frequencies are 400, 376 and 155 MHz respectively for ^1H and ^{19}F nuclei ($\pi/2$ pulses are respectively 8 and 7.5 ms). The self-diffusion measurements were performed with the pulsed field gradient stimulated echo and LED sequence using 2 spoil gradients (PFG NMR). The magnitude of the pulsed field gradient was varied between 0 and 55 G cm^{-1} (sinus shaped pulsed gradient); the diffusion time Δ between two pulses was fixed at 500 ms and the gradient pulse duration, δ, was set between 3 and 22 ms depending on the diffusion coefficient of the mobile species. This allowed us to observe the attenuation of spin echo amplitude over a range of at least 2 decades leading to a good accuracy (≤ 5 %) of the self-diffusion coefficient values. They were determined from the classic relationship $\ln(I/I_0) = -\gamma 2Dg2\delta 2(\Delta - \delta/3)$ where g is the magnitude of the two gradient pulses, γ is the gyromagnetic ratio of the nucleus under study and I and I_0 are the areas of the signals obtained with or without gradient pulses, respectively.

Results and discussion

Melting point

For applying ionic liquids in the PEMFC, their melting points should be lower than 130 °C. For the salts resulting from symmetrical amines and triflic acid, the measured melting points were found to be very high (Table 2).

Table 2 – *Thermal properties of synthesized salts based on primary amines*

$–NH_3^+$, T_f	Pr	iPr	Bu	iBu	MePrCH	$BuNH_3^+$, TFSI
mp (°C)	176	180	178	220	85	20
T_g (°C)	–	–	–	–	–25	–75

For triflate salts, both $PrNH_3^+$ and $iPrNH_3^+$ amines are of high symmetrical character and taking into account the similar melting points obtained, it can be concluded that ramification does not affect the melting point. The same is valid for $BuNH_3^+$ and $iBuNH_3^+$ amines. $MePrCHNH_3^+$ salt of triflic acid however, shows significant influence of symmetry on the melting point (85 °C). This salt is thus compatible with operation of PEMFC at 130 °C. Synthesis of $BuNH_3^+$, TFSI salt supported the previously reported data[13] that TFSI anion reduces the melting point comparing to triflate anion (from 178 °C for $BuNH_3^+$, T_f to 20 °C for $BuNH_3^+$, TFSI).

Thermal degradation

Degradation temperature of ionic liquids should be very high (at least > 150 °C) for their use in the PEMFC system. The salts containing fluorinated atoms showed high degradation temperatures.[8,14] Angell reported that thermal decomposition temperature of ILs depends on the pKa values of the starting amines and acids.[15] Therefore, better thermal stabilities of triflic acid salts (pKa = 0.23) are expected in comparison to sulphuric and phosphoric acids. Here, the thermal stability of ionic liquids was evaluated under helium atmosphere by using thermogravimetric analysis (TGA). Fig. 2 shows that $MePrCHNH_3^+$, T_f salt is thermally stable upon 350 °C.

High thermal stability demonstrates that the salt does not undergo degradation into its initial components (amine: bp = 33–91 °C and acid: bp = 162 °C).

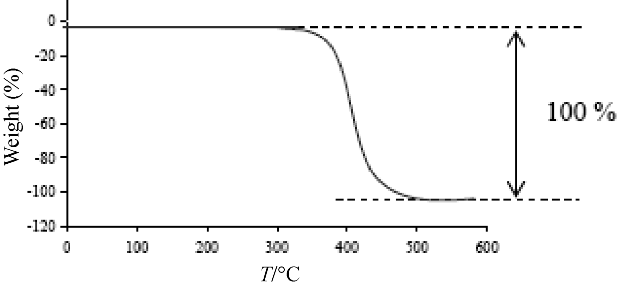


Fig. 2 – *Thermal degradation of $MePrCHNH_3^+$, T_f salt*

Thermal transitions

It is important to know thermal transitions between glassy and crystalline states of the ionic liquids. In general, the glass transition temperature must be sufficiently low for a noncrystalline (amorphous) salt.[16] For a great number of alkylimidazoliums with alkyl chains variable in length from butyl to decyl,[17] glass transition temperatures were found between –65 and –97 °C. For aliphatic ammoniums containing primary amines, only few values of T_g were reported. Angell[18] and Watanabe[19] could not determine T_g for ethylammonium and butylammonium with a series of anions including the triflate anion.

Here, measurements of T_g were taken with the DSC (Differential Scanning Calorimetry) modulated by scanning from –120 °C to 150 °C with a rate of 3 °C min^{-1}. Because the salts studied in the present work were extremely crystalline, some difficulties in T_g measurements were encountered. Therefore, the components were first heated to temperatures higher than their melting points, and then soaked quickly into the liquid nitrogen. This method inhibits the salt crystallization, maintains the amorphous state[20] and enables measurement of T_g values (Table 2).

Density

Densities of ionic liquids must be very high in order to obtain high salt concentrations in the ionic liquid which would in turn increase the charge carrier's number. A density of 1.45 g cm^{-3} was measured, which is in agreement with literature data (1 and 1.6[21,22]).

Viscosity

Being the reverse of fluidity, viscosity must be very low to induce high ionic mobility. Viscosity measurements were taken within a small temperature range, from the melting point up to 150 °C. For the substances having melting points of 85 °C, the viscosities could be measured only from 90 °C. The obtained viscosity values (Table 3) are in agreement with the Angell's work,[19] who presented viscosities of a series of primary ammoniums combined with different anions (at 120 °C, $BuNH_3^+$, HSO_4^- : 0.03 Pa s ; $EtNH_3^+$, HSO_4^- : 0.016 Pa s).

Table 3 – *Viscosity of $MePrCHNH_3^+$, T_f salt at various temperatures*

T (°C)	100	120	150
η (Pa s)	0.02118	0.01617	0.0131

Low viscosities obtained in this work are attributed to the weak cohesion forces and the electrostatic interactions (van der Waals and hydrogen bonds). These interactions are weak for the molecules containing fluorine atoms and for the cations with short alkyl chain.

Conductivity

One of the most important properties of ionic liquids is ionic conductivity. For the successful application of ionic liquids, their ionic conductivity should be very high. Specific conductivities were measured in the temperature range from 20 to 150 °C. At 130 °C which is the operating temperature of PEMFCs, specific conductivity of the triflate of methylbutylammonium is 13 mS cm^{-1} (Fig. 3). This value is close to those reported by Watanabe[20] who obtained the conductivity of about 20 mS cm^{-1} for quarternary ammoniums combined to HTFSI. For a series of imidazolium combined with different anions (HTFSI, triflate, acetate …) Bond[23] has obtained conductivity values between 2 and 14 mS cm^{-1}.

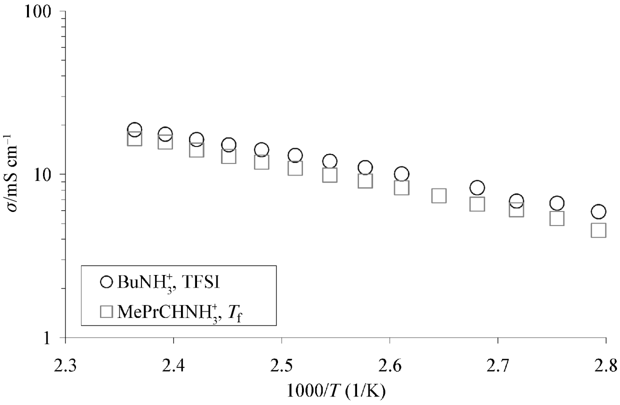


Fig. 3 – *Specific conductivities of* $MePrCHNH_3^+$, T_f *and Bu, TFSI salts in dependence on temperature*

Fig. 3 also shows that conductivity of MePrCHN, T_f (5 carbon atoms) is similar to BuN, TFSI (4 carbon atoms) salts. This means that conductivity of BuN, TFSI is not affected by the alkyl chain length or by presence of fluorine atoms. These two factors should result in higher conductivities for the second salt (BuN, TFSI). The similarity in the values, however, could be explained by the combination of the conductivity equation (eq. 1), the Stokes-Einstein equation (eq. 3) and the Nernst-Einstein equation (eq. 4) to the equation (eq. 5) that relates conductivity, σ, of ionic liquid and its viscosity, η:[10]

$$\sigma = F\,\Sigma C_i \mu_i = F(C_a \mu_a + C_c \mu_c) \tag{1}$$

In eq. (1), F is Faraday constant, while C_a, C_c, μ_a, and μ_c are concentrations and mobilities of anions and cations respectively.

$$C_a = C_c = y\,C \text{ where } C = d/W$$

$$\sigma = y\,F\,C(\mu_a + \mu_c) \tag{2}$$

In eq. (2), d is density, W is molecular weight and $0 < y < 1$ is degree of dissociation.

$$D_a = \frac{RT}{6\pi N_A \xi_a r_a \eta} \text{ and } D_c = \frac{RT}{6\pi N_A \xi_c r_c \eta} \tag{3}$$

In eq. (3), R is gas constant, T is temperature, N_A is Avogadro number, while D_a, D_c, ξ_a ,ξ_c, r_a and r_c are diffusion coefficients, micro-viscosity factors and Stokes radii of anion and cation, respectively.

$$D_a = \frac{\mu_a RT}{F} \text{ and } D_c = \frac{\mu_c RT}{F} \tag{4}$$

$$\sigma = \frac{yF^2 d\lfloor(\xi_a r_a)^{-1} + (\xi_c r_c)^{-1}\rfloor}{6\pi N_A W\,\eta} \tag{5}$$

Eq. (5) includes the correlation factor, ξ, which describes interactions between rotating ions in the salts. According to eq. (5), the conductivity of ionic liquid is related to its viscosity, molecular weight, density and Stokes radii of ions. Also, eq. (5) shows that in addition to viscosity, effects of the molecular mass and size on conductivity values are also important. Therefore, the conductivity of the ionic liquid with triflate could be similar to HTFSI (Fig. 3) because of its weak density resulting from small anion and lower molecular weight (237.24 g mol^{-1} for MePrCHN, T_f, and 354.29 g mol^{-1} for BuN, TFSI).

Diffusion coefficient

Kreuer[24] explained that the intermolecular proton transfer between protonated and unprotonated amine has a major role in the mechanism of protonic conductivity. Indeed, the conductivity is related to the concentration of charge carriers and intermolecular protonic transfer rate. Watanabe reported the studies on ammonium salts having two nitrogen atoms, *i.e.* 4,4'-trimethylenedipyridine[17] and imidazoliums.[25] He found that diffusion mechanism is managed by the combination of diffusion of protonated amines (vehicular mechanism) and the free proton hoping (from the ammonium salt dissociation) towards the other amine (Grotthus mechanism).[17] Comparison between monoamine system (pyridinium) and diamine system (imidazolium) was also carried out by Watanabe.[26] He showed that the cations diffuse more slowly in monoamine systems than in diamine systems, but the mechanism of conductivity was not discussed.

Here, diffusion coefficients were estimated by NMR-PGSE (echo of spin pulsated field). Diffusion coefficients of anion, amine and proton in the ionic liquid were calculated from the chemical shifts at various temperatures. The displacement of the anion is ensured by its fluorine atom, while that of the amine by its nitrogen atom. Fig. 4 shows that amine and anion diffuse together at the same rate, whereas the rate of the proton diffusion is much higher. This suggests that conductivity is ensured by important contribution of a proton jump from the ammonium to amine (intermolecular route) like in the Grotthus mechanism.

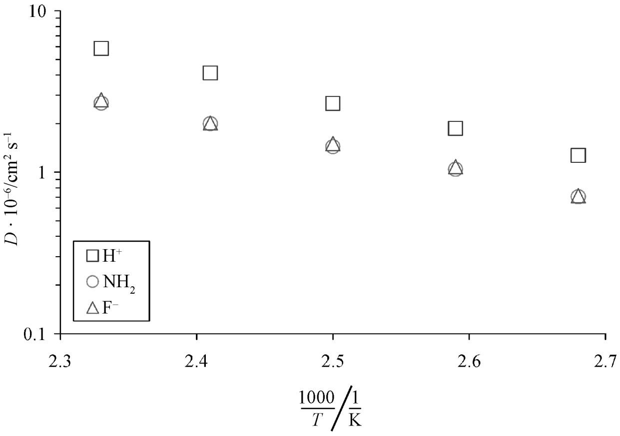


Fig. 4 – *Diffusion coefficients of proton, amine and anion of $MePrCHNH_3^+$, T_f salt in dependence on temperature*

The correlation between the structure of the ionic liquids and transport properties is not completely known.[6] Watanabe[20] reported that difference in the size between cation and anion results in the difference of their diffusion coefficients in the ionic liquid. The cation-anion interactions influence the ionic liquid viscosity which is related to the diffusion coefficients by the Stokes-Einstein equation (eq. 3).

The transport numbers of the cation and anion, t^+ and t^-, can be deduced from diffusion coefficients according to:

$$t^+ = \frac{D^+}{D^+ + D^-}; \quad t^- = \frac{D^-}{D^+ + D^-} \tag{6}$$

Fig. 5 shows $t^+ > t^-$ at all temperature and t^+ that ranges between $0.6 < t^+ < 0.7$.

Watanabe[20] observed similar t^+ (∼ 0.6) at 100 °C for imidazolium cation combined with TFSI. By comparison with the ionic liquid obtained by the combination of the same cation with BF_4^- anion, t^+ is 0.54. The transport numbers as well as diffusion coefficients are then related to the difference in the anion/cation size. In Fig. 5, t^+ is very high compared to t^- which is in accordance with the Grotthus mechanism.

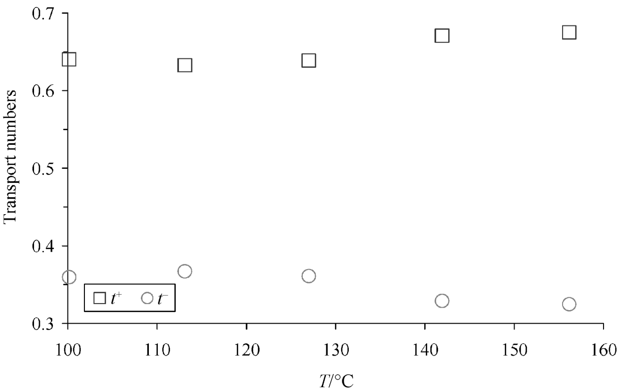


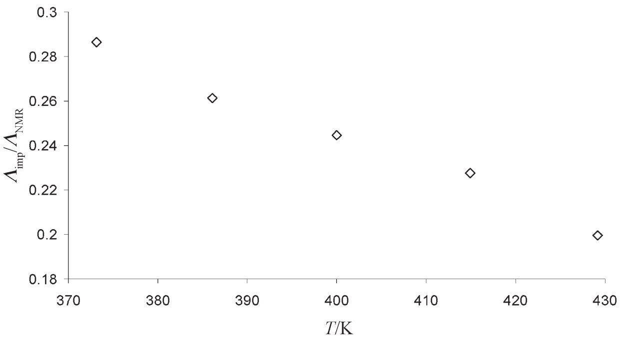
Fig. 5 – *Cationic and anionic transport numbers of $MePrCHNH_3^+$, T_f salt in dependence on temperature*

Degree of dissociation

The degree of dissociation is quantified as the ratio of molar conductivities, Λ, obtained in two ways. The first is to divide ionic conductivity by the molar concentration, Λ_{imp}, and the second is to use the Nernst-Einstein equation (eq. 4) and diffusion coefficients obtained from NMR-PGSE.[20]

$$\Lambda_{NMR} = \frac{N_A e^2 (D_c + D_a)}{kT} = \frac{F^2 (D_c + D_a)}{RT} \tag{7}$$

In eq. (7), e is electric charge on every ionic carrier and k is Boltzmann constant,. The calculated molar conductivity Λ_{NMR} is at all temperatures always higher than the experimental one Λ_{imp}. Indeed, Λ_{NMR} is calculated taking into account that all detected species obtained by NMR-PGSE contribute to molar conductivity, while calculation of Λ_{imp} is based on the migration of charged species under electric field. The ionic liquid can contain ion pairs, free ions and charged aggregates, where these last two forms contribute to the conductivities under electric field. Thus, the $\Lambda_{imp}/\Lambda_{NMR}$ ratio is correlated to the ionic associations in the ionic liquids. $\Lambda_{imp}/\Lambda_{NMR}$ ratio is usually lower than 1 what indicates that not all species which diffuse in the ionic liquid contribute to the ionic conduction. The charge carrier concentration is thus significantly lower than that of the salt in the ionic liquid. Watanabe[20] calculated the $\Lambda_{imp}/\Lambda_{NMR}$ ratio for a series of imidazolium, pyridinium, pyrrolidinium and quaternary ammonium compounds with TFSI and obtained the highest values for the aliphatic cations. The $\Lambda_{imp}/\Lambda_{NMR}$ ratio (Fig. 6) indicates the percent-



F i g . 6 – *Molar conductivity ratio* ($\Lambda_{imp}/\Lambda_{NMR}$) *of* $MePrCHNH_3^+$, T_f *salt in dependence on temperature*

age of the ions (charged species) that contribute to ionic conductivity. The ratio of 28 % at 100 °C and 20 % at 150 °C for $MePrCHNH_3^+$, T_f is obtained.

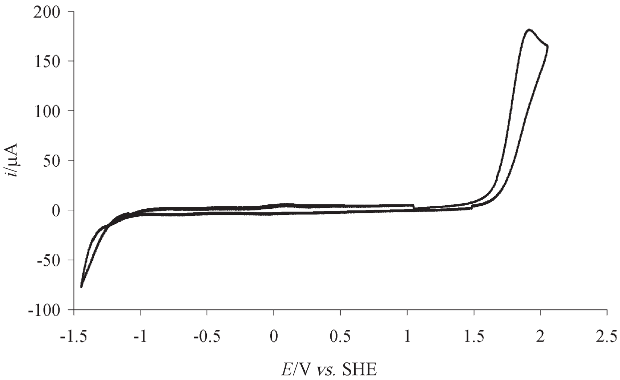
Contrary to what was observed by Watanabe,[20] $\Lambda_{imp}/\Lambda_{NMR}$ varied with temperature. The decrease of $\Lambda_{imp}/\Lambda_{NMR}$ with temperature implies a decrease of dissociation in the ionic liquid at higher temperature.

Electrochemical stability

It is well known that the broader the electrochemical window, the more stable is the compound. To have electrochemically stable ionic liquids and amines, it is therefore necessary that their reductions and oxidations occur at voltages higher than voltages of water decomposition.

The suggestion that conductivity of ionic liquids follows the Grotthus mechanism, indicates the participation of the starting amine in the overall conduction process, and so a partial dissociation of amines is always assumed. Oxidation of the amine produces a radical cation. This process is irreversible and occurs at 1.93 V/SHE (Fig. 7), which is a much higher value than the potential of water oxidation (1.23 V/SHE).

Fig. 7 also shows stability of the amine at the cathodic side because no reduction peak is observed. This kind of behavior is observed for all primary amines studied in this work, and their anodic peak potential values, E_{pa}, are listed in Table 4.



F i g . 7 – *Voltammogram of* $MePrCHNH_2$ *primary amine*

T a b l e 4 – *Oxidation potentials of primary amines*

$-NH_2$	Pr	iPr	Bu	iBu	MePrCH
E_{pa}/V vs. SHE	1.92	1.90	2.02	1.98	1.93

It can be seen in Table 4 that E_{pa} values are lower for the amines with higher length of the alkyl chain. This can be explained by the corresponding increase of the local electron density on the nitrogen atom, which in turn lowers the oxidation potential of the amine. Therefore, it is always important to control the substitution of the amine with respect to its electrochemical stability. For example, propylamine, which is the weakest substituted amine, should have the highest E_{pa}. Also, isopropylamine should have higher E_{pa} than isobutylamine. Taking into account E_{pa} values, the following ascending order of salts is expected to be formed: $MePrCHNH_2$ < $iBuNH_2$ < $BuNH_2$ < $iPrNH_2$ < $PrNH_2$. This order, however, was not observed experimentally, probably because of adsorption of these amines on the platinum surface.[27–29] Possible adsorption is supported by the characteristic shapes, *i.e.* by broadening of anodic peaks observed in voltammograms of $iBNH_2$ and $iPrNH_2$ (Fig. 8).

For ionic liquids, the limit at the cathodic side corresponds to reduction reaction of the ammonium cation. Fig. 9 shows a quasi-reversible reduction of $MePrCHNH_3^+$ cation.

All the synthesized salts are reduced at nearly the same potential value which was already observed for other ionic liquids[19] (Table 5). Generally, all the synthesized salts were sufficiently stable in the domain of fuel cell operation, which is supported by data in Table 5.

Impregnation in Nafion®

Behavior of the $MePrCHNH_3^+$, T_f ionic liquid in the fuel cell was tested by its incorporation in the Nafion® membrane. The membrane is the central part of the fuel cell that allows the proton exchange and separates two gases O_2 and H_2. Incorporation of the ionic liquid is made under inert atmosphere by heating at temperatures above the melting point of ionic liquid and glass transition of Nafion®. Such heating facilitates incorporation of the ionic liquid into the form of the ionic clusters. The obtained incorporation (swelling) level, τ, of the methylbutylammonium triflate in Nafion is 40 %.

Incorporation of the PIL within the Nafion® in acid form (Fig. 10) causes liberation of acid at high

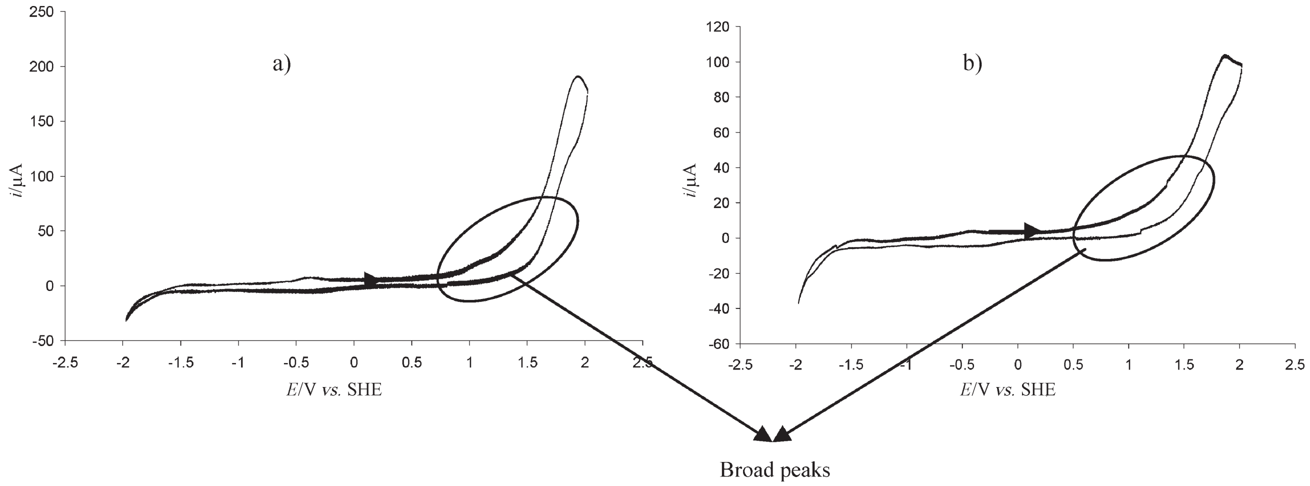


Fig. 8 – *Voltammogramms of iBuNH$_2$ (a) and iPrNH$_2$ (b) primary amines*

Table 5 – *Cathodic half-wave potentials and potential differences between anodic and cathodic current peaks of synthesized salts*

$-NH_3^+$, T_f	Pr	iPr	Bu	iBu	MePrCH	$BuNH_3^+$, $TFSI^-$
$Ec_{1/2}$/V vs. SHE	–0.65	–0.66	–0.66	–0.60	–0.68	–0.69
ΔE_{pc}/mV	290	310	310	260	310	320

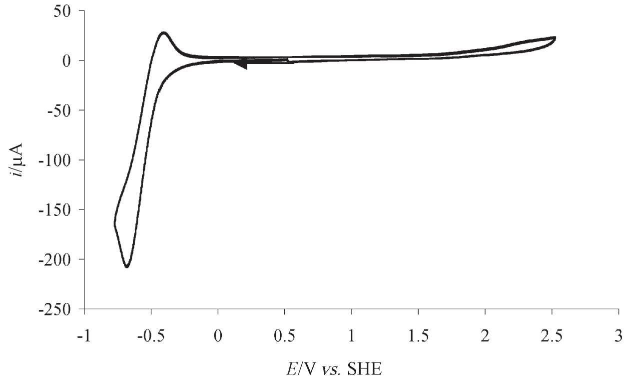
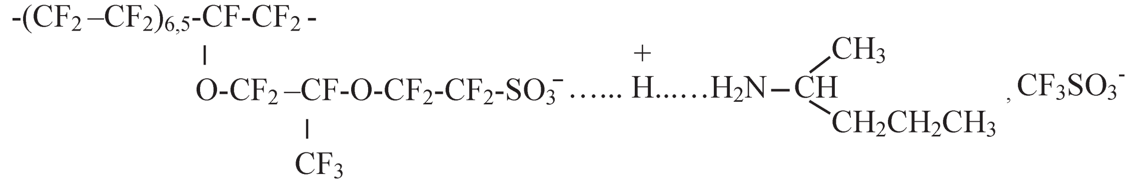


Fig. 9 – *Voltammogramm of MePrCHNH$_3^+$, T_f salt*

temperatures,[3,31] which affects the conductivity of the membrane. The sulphonate groups of Nafion® are firstly neutralized by the initial amine. Fig. 11 shows the cation exchange between the amine and the proton of the final sulphonic group in Nafion®.

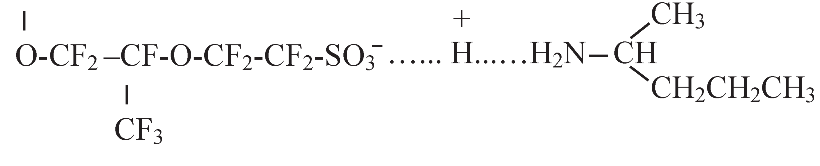
Conductivity of impregnated membrane

Shmidt[32] reported that the conductivity of dry Nafion® 117 decreases with an increase of temperature from about 0.95 mS cm^{-1} at 40 °C to 0.01 mS cm^{-1} at 122 °C. This was explained by the evaporation of residual water that is necessary for proton conduction in the Nafion®. The measured



$$\begin{array}{l} -(CF_2-CF_2)_{6,5}-CF-CF_2- \\ \qquad\quad | \\ \qquad\quad O-CF_2-\underset{\underset{CF_3}{|}}{CF}-O-CF_2-CF_2-SO_3^-\ldots\ldots\overset{+}{H}\ldots\ldots H_2N-CH\begin{matrix}\nearrow CH_3\\ \searrow CH_2CH_2CH_3\end{matrix}\ ,\ CF_3SO_3^- \end{array}$$

Fig. 10 – *Nafion® impregnated (swollen) by MePrCHNH$_3^+$, T_f salt*



$$\begin{array}{l} -(CF_2-CF_2)_{6,5}-CF-CF_2- \\ \qquad\quad | \\ \qquad\quad O-CF_2-\underset{\underset{CF_3}{|}}{CF}-O-CF_2-CF_2-SO_3^-\ldots\ldots\overset{+}{H}\ldots\ldots H_2N-CH\begin{matrix}\nearrow CH_3\\ \searrow CH_2CH_2CH_3\end{matrix} \end{array}$$

Fig. 11 – *Nafion® neutralised by MePrCHNH$_2$ amine*

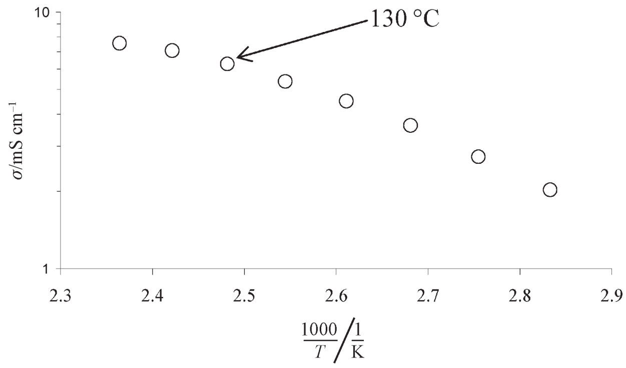


Fig. 12 – *Specific conductivity of Nafion® swollen by $MePrCHNH_3^+$, T_f salt in dependence on temperature*

conductivity of the impregnated membrane increases with temperature (Fig. 12).

For temperatures higher than 80 °C, the measured conductivities reached values of about 6.3 mS cm^{-1} at 130 °C and 7.6 mS cm^{-1} at 150 °C, thus exceeding the values of pure, dry Nafion®. These values are better than the conductivity values obtained by Proulx[3] and Schmidt[32] for Nafion® impregnated by ILs based on imidazolium[3,32] and pyrrolidinium[32] cations combined with perfluorinated anions (triflate, BF_4^-, PF_6^-, TFSI and FAP: $(CF_2CF_3)_3F_3P^-$). Indeed, the best conductivity obtained by Schmidt was 1 mS cm^{-1} at 120 °C for FAP imidazolium. Proulx[3] showed a conductivity of 5.1 mS cm^{-1} for triflate imidazolium at 120 °C (his IL presents a conductivity of 60 mS cm^{-1} at 150 °C in the pure state).

The conductivities of several Nafion®-117 membranes with different levels of ionic liquid incorporation were also measured (Fig. 13).

Conductivity at 130 °C was improved by the incorporation of more ionic liquid in the membrane (from 0.01 mS cm^{-1} at 10 %, up to 6 mS cm^{-1} at 40 %). The extrapolation of the conductivity curve to the incorporation level of 100 % resulted in the conductivity value of 8 mS cm^{-1} (Fig. 14).

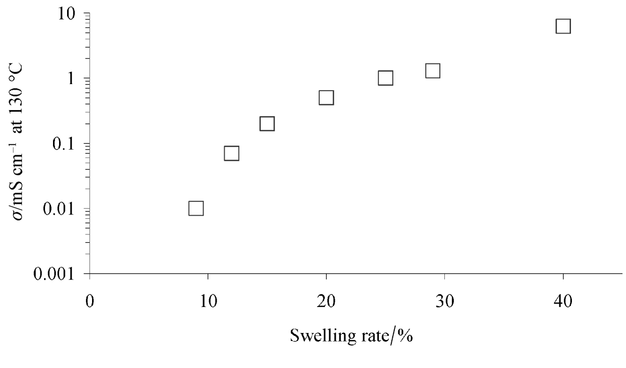


Fig. 13 – *Specific conductivity at 130 °C of Nafion® swollen by $MePrCHNH_3^+$, T_f salt in dependence on the swelling rate*

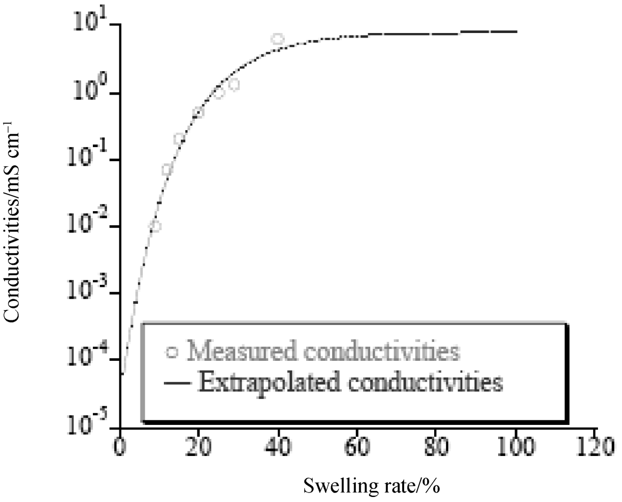


Fig. 14 – *Extrapolation of Fig. 13*

The representation of σ/τ function shows that the degree of dissociation of the ionic liquid in the membrane is not constant (Fig. 15).

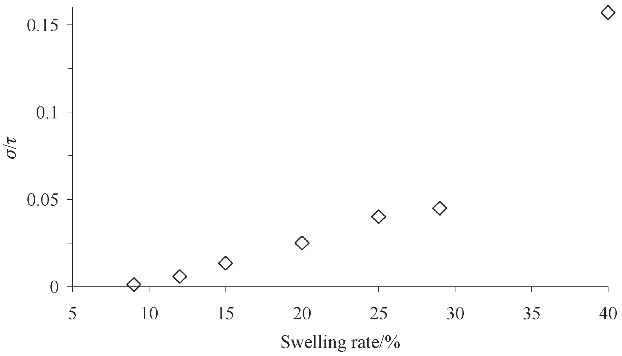


Fig. 15 – *Ratio between conductivity and swelling level as a function of the swelling rate*

When τ increases, dissociation also increases. Two zones are clearly presented in Fig. 15. At low swelling levels, dissociation is weak, and polarity of the medium is partially determined by the Nafion®. At high swelling levels, dissociation plays an important role and polarity is principally determined by the ionic liquid. This suggests that the polarity of the medium depends on the nature of the environment.

Conduction mechanism

The diffusion coefficient of every species in the impregnated membrane was also determined by NMR-PGSE. In comparison with Fig. 4, Fig. 16 shows that ionic diffusion in the membrane is slower (by a factor of 10) than in the ionic liquid and that diffusion coefficients of protons and amines are almost identical.

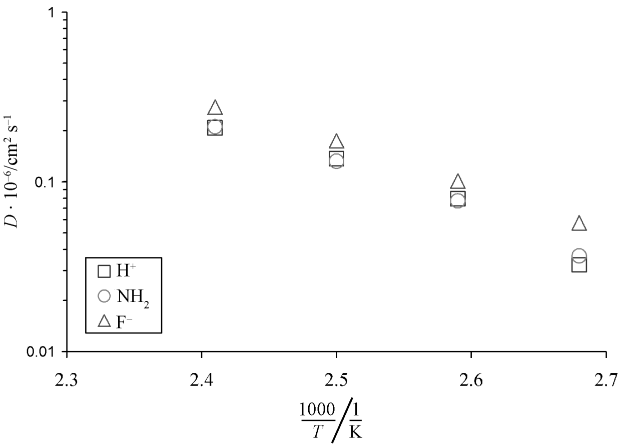


Fig. 16 – *Diffusion coefficients of Nafion® swollen by MePrCHNH$_3^+$, T_f salt in dependence on temperature*

This suggests that ionic mobility is higher in the ionic liquid than within polymer channels and that the diffusion process is affected when the ionic liquid is incorporated into the membrane even at levels of 40 %. On the other hand, Fig. 17 suggests that the anionic character of the Nafion® contributes to the “retaining” of the cationic species ($t^+ < t^-$), probably by electrostatic phenomena.

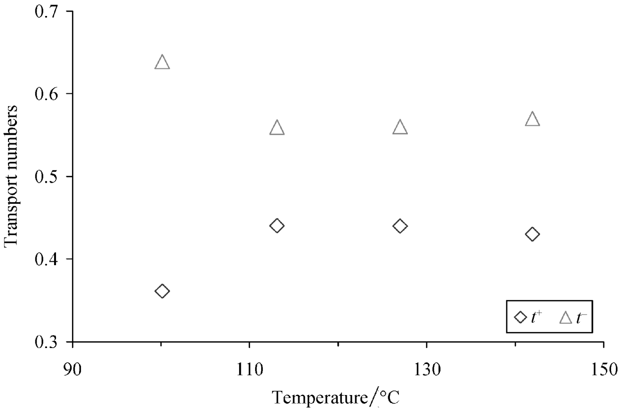


Fig. 17 – *Cationic and anionic transport numbers of Nafion® swollen by MePrCHNH$_3^+$, T_f salt in dependence on temperature*

Thermal transitions

The results of DSC analysis indicate various processes in acid, neutralised and impregnated forms of Nafion® (Fig. 18). Moore *et al.*[40] demonstrated three transitions in Nafion®-H$^+$, α, β and γ at 100, –20 and –80 °C respectively. It has also been shown that γ-transition is not dependent; α-transition is only slightly affected, while β-transition is strongly dependent on the nature of the alkylammonium exchanged with H$^+$.[40]

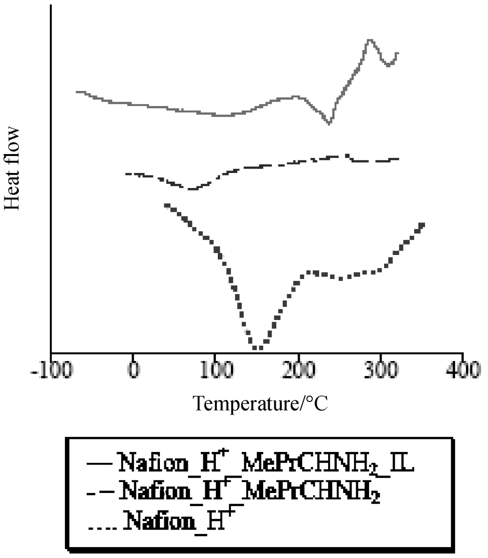


Fig. 18 – *Thermogramm of Nafion® in its acid form, neutralised by MePrCHNH$_2$ amine and swollen by MePrCHNH$_3^+$, T_f salt*

Fig. 18, however, does not show all transitions of the Nafion®-H$^+$ curve, but at higher temperature (250 °C) the transitions corresponding to the melting of crystalline domains or polymer degradation[34] are noticed. Neutralization of Nafion® by amine increases the hydrogen bonds in the main backbone and increases T_β (75 °C) while T_α is not affected. This is confirmed by the thermogravimetric analysis of Nafion®-H$^+$ and Nafion® neutralized by amine (Fig. 19).

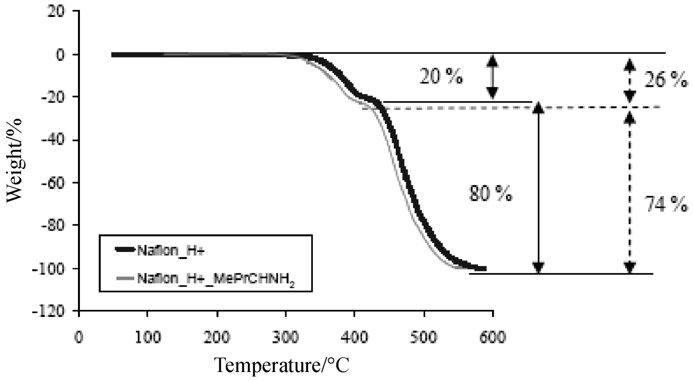


Fig. 19 – *Thermal degradation of Nafion® in its acid form and neutralised by MePrCHNH$_2$ amine*

Since DSC analysis is not a fully reliable method to estimate entire polymer transitions, a dynamic mechanical study was applied (Fig. 20). For the neutralised Nafion® form, the process corresponding to β-transition at about 30 °C is indicated as the stage of molecular rearrangement inside the clusters of the polymer.[33] This is followed by α-transition at 113 °C. (118 °C for Nafion®-H$^+$).

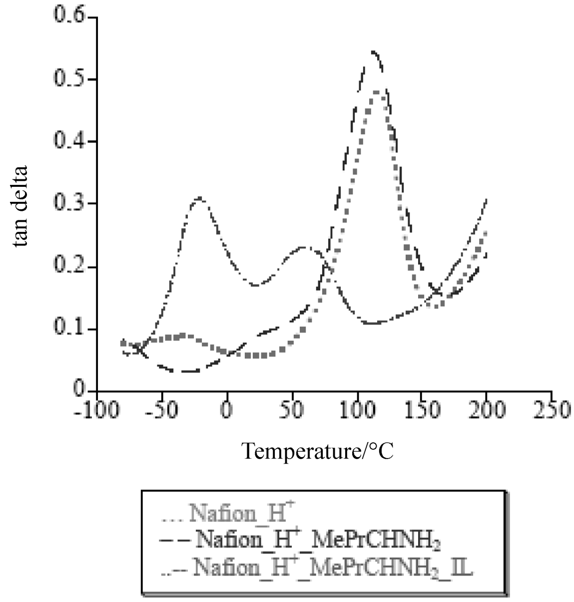


Fig. 20 – *Thermal transitions of Nafion® in its acid form, neutralised by MePrCHNH$_2$ amine and swollen by MePrCHNH$_3^+$, T$_f$ salt*

The transitions in the polymer are also affected by the ions and absorption of the organic solvent.[41] Consequently, the curve of the impregnated membrane shows decrease in T_β value (–20 °C) and T_α (60 °C). In correlation with Schmidt results on Nafion impregnated by ionic liquids (fluorinated alkylimidazolium and alkylpyrrolidinium),[32] and Brazel studies on the plasticizing polymers (polymethyl-methacrylate),[42,43] the Nafion®-PIL behaviour seems to be due to the plasticizing effect of the ionic liquid which involves mobility of segments. Gierke explains that an increase in the absorbed solvent by the membrane involves a high number of sulphonic groups formed in clusters that increases in size and involves a larger clusters organization.[35]

Thermal degradation

Thermal degradation, measured as a variation of weight with change of the temperature is indicative for a loss of sample molecules. For acid neutralized (Fig. 19) and swollen forms of Nafion® (Fig. 21), a quite similar behavior is observed.

For the pure Nafion® (Fig. 19), the first deterioration of 20 % starting from 390 °C is followed by the second one of 80 %. At 550 °C, the polymer is completely degraded. For the Nafion® neutralized by amine similar behaviour is observed, although degradation occurs at lower temperatures. Also, the first deterioration is more important for the neutralized form than for the acid form of Nafion®, because the cation degradation produces more H_2O and CO_2 which are released between 25 and 400 °C.[34] Concerning the impregnated membrane in Fig. 21, a slight mass loss starting from 200 °C was observed. This corresponds to the presence of water, probably absorbed by Nafion® before starting the measurement. However, this stage represents only a loss of 2 % in weight. At higher temperatures, a mass loss of 30 % is observed, corresponding to the evaporation of SO_2 and CO_2 coming from the swollen salt and neutralized membrane. The second mass loss of 50 % is due to the degradation of the fluorinated compounds. The comparison between pure ionic liquid and ionic liquid incorporated in Nafion® in Fig. 21 shows better thermal stability for the first. The mass loss starts from 340 °C and occurs in only one stage. Due to all previously stated, it could be deduced that the impregnated membrane is stable in a broad temperature window (20 °C – 250 °C) which is in agreement with the literature.[34]

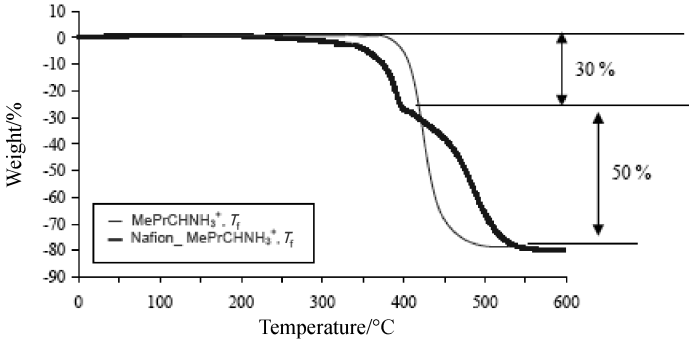


Fig. 21 – *Thermal degradation of Nafion® swollen by MePrCHNH$_3^+$, T$_f$ salt compared to pure ionic liquid*

Mechanical properties

Mechanical properties of the polymer are related to the content of ions occupying a very low volume in the polymer.[36] The Young, or storage modulus decreases with time, and informs about rigidity.[37] Tang *et al.*[38] have shown that with increasing temperature, the amorphous domain decreases leading to a weaker Young modulus. They also compared mechanical properties of the as-received and treated Nafion® showing weaker Young modulus for the treated membrane than that for the untreated membrane. The counter-ions affect also mechanical properties and the bulk counter-ion decreases the Young modulus even more.[37,39,44] Similar behaviour is expected for the membrane in the acid form and after neutralization with amine. Fig. 22 shows lower storage modulus for neutralized membrane, and dramatic effect of the swelling to the mechanical properties.

Ionic liquid reduces mechanical properties up to 7 MPa at 80 °C to 2 MPa at 130 °C. This is due to the ionic liquid plasticizing effect on the polymer

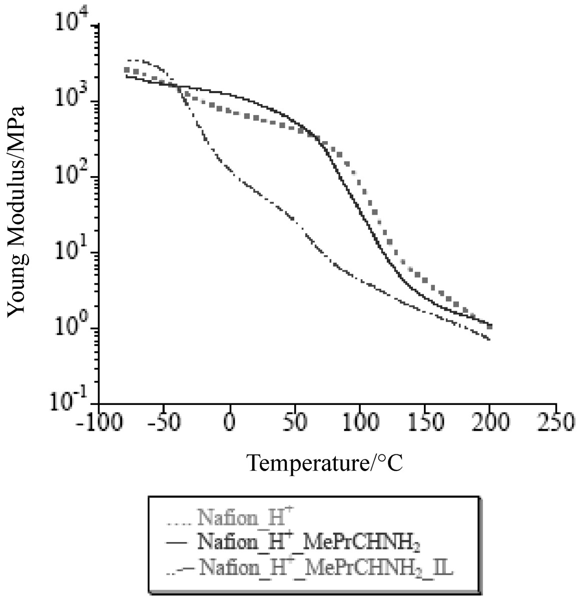


Fig. 22 – *Young (Storage) modulus of Nafion® in its acid form, neutralised by $MePrCHNH_2$ amine and swollen by $MePrCHNH_3^+$, T_f salt*

reported by Brazel *et al.*[42,43] The plasticizing effect of the absorbed ionic liquid may be attributed to incorporation of cations with flexible alkyl side chains (propyl or pentyl), and/or partial disruption of H bonds generated by the sulfonic acid groups in the hydrophilic clusters by the mostly hydrophobic and bulky anions. Again, the hydrophobic and voluminous MePrCH anion seems to have a high impact on plasticizing of the Nafion® matrix. Indeed, from the first transition β, there is a significant fall of the storage modulus from 2000 to 100 MPa.

Conclusions

After having synthesized various ammonium salts by neutralization of primary amines with triflic acid and/or HTFSI, it was shown that only the salts resulting from asymmetrical cations or TFSI anion exhibited melting points lower than 120 °C. In addition to their thermal stabilities beyond 340 °C, this makes only the $MePrCHNH_3^+$, T_f and $BuNH_3^+$, TFSI salts compatible for utilization as additives in PEMFC electrolytes at 130 °C.

The electrochemical study showed that oxidation of the prepared salts by molecular oxygen can not take place (potential oxidation higher than 1.23 V/SHE), while concerning the cathodic behavior, the reduction of the proton (associated to the amine) is in strong correlation with the basic character of the amine. Conductivities of the salts follow the Grotthus mechanism and are high enough for their possible applications in the fuel cells.

The results obtained after incorporation of $MePrCHNH_3^+$, T_f salt within the Nafion® membrane showed very good Nafion®/salt compatibility. Ionic conductivity of the impregnated membrane was about 7 mS cm^{-1} at 130 °C, which was still lower than conductivity values of the hydrated Nafion® 117. Ionic conductivity of dry Nafion® upon substitution of water by the ionic liquid as a dipolar medium improved by a factor of about 100.

Mechanical properties of the Nafion® decreased with incorporation of ionic liquid, while conductivities of ionic liquids decreased upon insertion into Nafion®. At 130 °C, there is no conduction for the acid form of Nafion® (as used actually), but for the Nafion® ionic liquid form, the conductivity is promising.

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