



## Proton-conducting ionic liquid-based Proton Exchange Membrane Fuel Cell membranes: The key role of ionomer–ionic liquid interaction

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### ABSTRACT

The paper deals with the synthesis and characterisation of proton-conducting ionic liquids (PCILs) and their polymer electrolytes obtained by blending modified Nafion membranes with different concentrations of PCILs. The PCILs are obtained by the neutralization of triethylamine with different organic acids. The first part of the paper studies the influence of acidity and acid structure on PCIL thermal and electrochemical performance, while the second part examines membrane conductivity and reveals it to depend more on PCIL structure than on its intrinsic conductivity. At 130 °C, conductivities exceeding 10 mS cm<sup>-1</sup> were obtained in fully anhydrous conditions.

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### 1. Introduction

Until recently, lithium batteries have been mainly used in portable electronic applications. But since the double success, in terms of performance and attractivity, of Toyota's pioneering hybrid car, i.e. the Toyota Prius powered by nickel-metal hydride batteries, considerable attention is now being focused on lithium batteries. However, one of the main drawbacks is the high cost of current lithium-ion batteries dedicated to the electronic market. In addition, developing a consumer market in electric and hybrid cars requires very high safety standards, but recently confidence in Li-ion batteries has been shaken by incidents occurring in laptop Li-ion batteries. Several national policies have recently promoted the development of high capacity batteries dedicated to electric/hybrid cars. These developments are illustrative of the perpetual yo-yo movement between fuel cells and batteries which has been going on for the last 15 years, reflecting the fact that none of these technologies is currently mature enough to meet the requirements imposed by a very large consumer market. The Proton Exchange Membrane Fuel Cell (PEMFC) and Direct Alcohol Fuel Cell (DAFC) address a wide range of applications from portable electronics to

transportation and electricity production. In portable electronics and hybrid/electric cars there is an indisputable overlap between PEMFCs and lithium batteries. Once a satisfactory solution has been found for fuel storage, the main advantage of PEMFCs vs. lithium batteries in electric cars is expected to be their greater safety. In transportation applications, however, they should always be used with batteries in order to take advantage of their complementarities. On the other hand, for sustainable electricity production applications, they do not compete with batteries but rather with high-temperature fuel cells, namely SOFCs (Solid Oxide Fuel Cells). While the upper operating temperature of 80 °C of current PEMFCs is sufficient for certain markets, it is not suited to either electric vehicles or electricity production. In the latter case, the modularity of PEMFCs might make them good candidates provided their operating temperature can be increased. This would favour heat-electricity cogeneration, with the heat produced being more easily recovered at high temperature.

Currently, the PEMFCs with the best performance are based on membranes and electrode active layers made of perfluorinated ionomers, most of which belong to the Nafion<sup>®</sup> family. Such PEMFCs are limited to an upper operating temperature close to 80 °C, with ionomer performance dropping sharply at higher temperatures. Since the electric yield of a PEMFC is no more than 50%, the thermal management of a PEMFC in a small- to medium-size car is a real issue. Therefore, for most car manufacturers, the

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upper operating temperature needs to be increased from 80 to 120 °C.

It thus appears that two potential mass-markets require a substantial increase in the operating temperature of PEMFCs. To obtain an increase up to at least 120 °C, the PEMFC would either have to be highly pressurized so as to maintain sufficient relative humidity in the membrane–electrode-assemblies, or the current membranes would need to be replaced by membranes that are highly conductive in the anhydrous state. The use of composite membranes including hygroscopic fillers cannot provide sufficient conductivities in these conditions. Polymers, whose monomer repeat units are Lewis bases, can be easily blended with strong acids. Thus poly(oxyethylene)/phosphoric acid blends provide conductivity maxima of the  $\text{mS cm}^{-1}$  level [1]. As for poly( $\gamma$ -aminopropyl) siloxane blended with 10 mol% of triflic acid, it reached  $10 \text{ mS cm}^{-1}$  at 120 °C [2]. Despite their high conductivities, these proton-conducting polymers were initially intended to be used as polymer electrolytes for electrochemical windows and were not designed for implementation in PEMFCs. They would most probably not meet the requirements of a high-temperature PEMFC (HT-PEMFC), particularly in terms of chemical stability. It was subsequently proposed to blend polybenzimidazole (PBI), a high-performance polymer, with phosphoric acid [3]. The related membranes have unquestionable assets, such as their expected low cost and the thermostable nature of the PBI host polymer. Obtaining highly conductive PBI membranes assumes, however, a high phosphoric acid uptake, which can result in dramatic degradation both of the membrane (mechanical properties) and the electrodes [4].

More recently, the use of proton-conducting ionic liquids (PCILs) was proposed in order to ensure high anhydrous proton-conductivities while maintaining sufficient thermal stability. This domain has since aroused a great deal of interest with a view to application in HT-PEMFCs [5–19].

The paper is divided into two parts. The first part deals with the synthesis and physico-chemical characterisation of PCILs obtained by the neutralization of triethylamine with several organic acids. The main objective of this part is to compare the influence of acid nature on the thermal and electrochemical performances of the PCILs. The second part focuses on the characterisation of the ionomer/PCIL membranes. The more stable PCILs were blended with neutralized Nafion 117. Their conductivities and mechanical properties are discussed.

## 2. Experimental

### 2.1. Products

Trifluoromethanesulfonic acid (TF), acetic acid (AA), methanesulfonic acid (MS), benzoic acid (BA) and perfluorobutanesulfonic acid (PFBu) were purchased from Aldrich and used as received. Perfluorooctane sulfonic acid (PFOc) was obtained by hydrolysis of perfluorooctane sulfonyl chloride. Triethylamine (TEA) and organic solvents were distilled before use. *Nomenclature*: AA-TEA: triethylammonium acetate; TFA-TEA: triethylammonium trifluoroacetate; TF-TEA: triethylammonium trifluoromethanesulfonate; PFBu-TEA: triethylammonium perfluorobutane sulfonate; PFOc-TEA: triethylammonium perfluorooctane sulfonate; AB-TEA: triethylammonium benzoate.

### 2.2. Proton-conducting ionic liquid (PCIL) syntheses

All PCILs were synthesized by reacting the corresponding acid with freshly distilled TEA. The MS-TEA, TF-TEA, and PFBu-TEA were synthesized using water as the solvent. 10 ml of acid was added to the bottom flask containing 100 ml of cold water. Then the mix-

ture was cooled by immersing the bottom flask in an ice bath. The mixture was stirred for at least 10 min, after which the acid was neutralized with triethylamine. The pH of the bottom flask solution was checked and the addition of triethylamine was stopped when the pH reached 8. The synthesis of PFOc-TEA was carried out in 50/50 (v/v, ethanol/water) following the same protocol as before. The water or ethanol/water and amine excess was eliminated under vacuum in the case of MS-TEA and TF-TEA, or by lyophilisation in the case of PFBu-TEA and PFOc-TEA. PCIL purification was performed using different approaches. In the case of MS-TEA and TF-TEA, the concentrated PCIL was solvated in 100 ml of methanol and then the solution was filtered on a carbon active column and the methanol removed by evaporation. The PFBu-TEA and PFOc-TEA were crystallized from a mixture of acetonitrile and diethyl ether (50/50). The resulting PCILs were dried for 48 h at 130 °C under vacuum.

The synthesis of AA-TEA, TFA-TEA and BA-TEA was performed in diethyl ether. The AA-TEA and TFA-TEA were purified by distillation at 150 and 210 °C, respectively. The AB-TEA was dried at 50 °C under vacuum.

PCIL water content was checked by Karl Fisher measurements and for all PCILs it was lower than 50 ppm.

PCIL purity was then checked by NMR, using a Bruker WM 250 spectrometer operating at frequencies of 250 MHz for the  $^1\text{H}$  and 235.3 MHz for  $^{19}\text{F}$ . The samples were dissolved in  $\text{CDCl}_3$ . Peak assignments of PCILs were carried out by reference to the starting amines and acids.

### 2.3. Cyclic voltammetry

All electrochemical measurements were made under an argon atmosphere in a dry glove box. Cyclic voltammetry (CV) experiments were performed using an Autolab potentiostat/galvanostat. The standard three-electrode electrochemical cell was used. The reference electrode was Ag wire/0.01 M  $\text{AgNO}_3$  in  $\text{CH}_3\text{CN}$  0.1 M  $\text{Bu}_4\text{NClO}_4$ . Potentials can be converted to the SHE (Standard Hydrogen Electrode) system by adding 0.548 V. The working electrode (5 mm in diameter) was a platinum disk polished with  $2 \mu\text{m}$  diamond paste (Mecaprex Presi). For experiments carried out with pure ionic liquid, the  $\text{Ag}^+/\text{Ag}$  reference electrode was separated from the PCIL by an intermediate compartment containing the same PCIL. This device was checked using ferrocene ( $E_{1/2} = 0.09 \text{ V}/\text{Ag}^+/\text{Ag}$ ).

### 2.4. Thermal analysis

Glass transition temperatures,  $T_g$ , melting temperatures,  $T_m$ , and crystallization temperature,  $T_c$ , were measured in nitrogen flow using a TA Instruments DSC 2920 modulated DSC. Around 10 mg of the sample was placed in a DSC aluminium crucible in a glove box. In a typical procedure, the samples were cooled rapidly to  $-100 \text{ °C}$  and then heated at a rate of  $5 \text{ °C min}^{-1}$  up to  $200 \text{ °C}$ . The oscillation period was 60 s and its amplitude was  $\pm 0.6 \text{ °C}$ .  $T_g$ ,  $T_m$  and  $T_c$  were taken as the inflection points of the increment of specific heat at respectively the glass–rubber transition and the onset of the melting or crystallization peak.

Thermogravimetric measurements (TGA) were carried out using a Netzsch STA409 thermal analyzer. Around 50 mg of the sample was heated from room temperature up to  $400 \text{ °C}$  at  $10 \text{ °C min}^{-1}$  in an air flow. The degradation temperature,  $T_d$ , corresponds to a 5% weight loss.

### 2.5. Rheometry

Rheometrical measurements were performed using a TA ARG2 rotational rheometer. Viscosity was determined through controlled

shear measurements using both parallel plates and cone and plate geometry. Viscosity measurement under shearing involves imposing a shear rate  $\dot{\gamma}$  ( $\text{s}^{-1}$ ) on the sample, and measuring the resulting shear stress  $\tau$  (Pa). The viscosity  $\eta$  (Pa s) can be calculated by dividing the shear stress by the shear rate.

$$\eta = \frac{\tau}{\dot{\gamma}}$$

Depending on the temperature, different geometries have to be used. In the first case, the ionic liquids were characterised in a temperature range between ambient and 60 °C, controlled through a Peltier effect heating plate. The diameter of the plate was such that a 60 mm cone with 1° truncature could be used, thus allowing accurate measurements to be performed. For temperatures above 60 °C, an oven was used with the rheometer. Due to the oven inner diameter, these measurements were associated with 25-mm diameter parallel plate geometry, with a 1 mm gap between the two plates.

As the ionic liquids tested have low viscosities, the rheological tests were based on continuous flow measurements, conducted in a dry nitrogen atmosphere. Due to the high hydrophilic nature of the PCILs, a dry atmosphere must be used to avoid water pollution, which would strongly impact on viscosity.

## 2.6. NMR experiments

NMR experiments on the pure PCILs, i.e. free of any added solvent, were carried out on a Bruker Avance NMR 400 spectrometer equipped with a broadband probe with z-axis gradient for the measurement of  $^1\text{H}$  and  $^{19}\text{F}$  spectra and the determination of  $^1\text{H}$  and  $^{19}\text{F}$  diffusion coefficients. Temperatures were controlled within the 300–420 K range with a Bruker BVT3000 system ( $\pm 1$  K regulation). The temperature was calibrated before each set of measurements by using the standard procedure with a reference ethylene glycol sample. PCILs were introduced in 4-mm diameter NMR tubes and sealed in a glove box under argon in order to avoid any contact with moisture. Narrow tubes were chosen in order to avoid convection movements within these low viscosity liquids.

Self-diffusion coefficients were determined with the pulsed field gradient stimulated echo and LED sequence using 2 spoil gradients. Self-diffusion coefficients were determined, as in a previous paper [20], from the classical relationship  $\ln(I/I_0) = -\gamma^2 D g^2 \delta^2 (\Delta - \delta/3)$  [21] where  $g$  is the magnitude of the two gradient pulses,  $\Delta$  is the time interval between these pulses,  $\delta$  is their duration,  $\gamma$  is the gyromagnetic ratio of the nucleus under study and  $I$  and  $I_0$  are the areas of the signals obtained respectively with and without gradient pulses. The magnitude of the pulsed field gradient was varied between 0 and 45  $\text{G cm}^{-1}$ ; the diffusion time  $\Delta$  between two pulses was fixed at 200 ms, and the pulse duration  $\delta$  was set between 3 and 20 ms, depending on the diffusion coefficient of mobile species.  $\pi/2$  pulse widths were calibrated to 8.5 and 17.5  $\mu\text{s}$  for  $^1\text{H}$  and  $^{19}\text{F}$ , respectively (12.5 and 9  $\mu\text{s}$  on the AV360 spectrometer).

## 2.7. Membrane elaboration

First the Nafion® 117 membrane was immersed in a 2 M  $\text{HNO}_3$  aqueous solution and heated at water reflux temperature for 2 h in order to recover all the Nafion acidic functions (Naf-H<sup>+</sup>). Then, the acidified Nafion membrane, washed several times with deionised water, was neutralized by triethylamine (TEA). Neutralization was performed by immersing the membranes at room temperature for 24 h in a 50/50 (v/v) mixture of ethanol and 4 M aqueous solution of TEA. The membranes were then washed with pure water and dried for 48 h under vacuum at 130 °C. Then the neutralized membranes were transferred to a glove box. The dried neutralized membranes were immersed in the corresponding PCIL heated to 80 °C and PCIL uptake was measured at different times. The PCIL swollen mem-

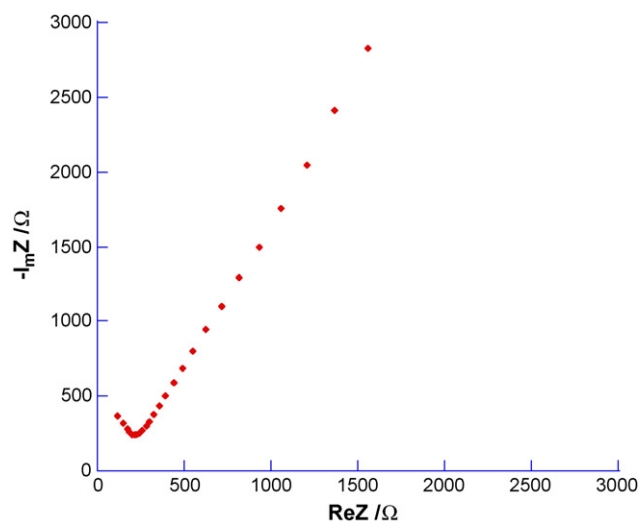


Fig. 1. Nyquist plot of Naf-TEA + MS-TEA (25% MS-TEA) at 100 °C connected from the set-up impedance.

branes were removed from the PCIL and kept in the glove box at room temperature for at least a week. The weight of the membranes was checked every 24 h over a week in order to evaluate membrane stability, and more specifically PCIL release from the membrane.

## 2.8. Conductivity measurements

Conductivities were determined by electrochemical impedance spectroscopy using an HP 4192A Impedance Analyser in the frequency range 5 Hz to 13 MHz.

A conductivity cell consisting of platinum electrodes was filled by the PCIL and closed in a glove box. The cell constant of ca.  $1 \text{ cm}^{-1}$  was determined using a standard KCl aqueous solution. The measurements were carried out from 20 °C up to a maximum temperature of 150 °C, the temperature being equilibrated for 2 h before each measurement.

The membranes were placed between two stainless steel electrodes under argon (in glove box) in a Swagelok cell with Teflon joints and spacers, and measurements were performed from 20 to 150 °C. The temperature was equilibrated for 2 h before each measurement.

Membrane thickness was determined with a Digimatic MDG-25SB micrometer by placing the membrane between two discs.

The spectra were recorded between 13 MHz and 5 Hz. Due to the high conductivity of PCIL and their membrane, at high frequency the resistive contribution of the set-up to the overall resistance (leads and connections) may range from 1 to 10% of the high frequency response of the membrane. For this reason, the impedances measured are corrected from the set-up impedance measured in the same frequency range. This impedance can be represented, below 4 MHz, using an equivalent circuit consisting of an inductance of 5  $\mu\text{H}$  associated with a resistance of 1.3  $\Omega$  in series. The resistance of the membrane is taken at the high frequency intercept with the real axis in the Nyquist plot (Fig. 1), which is usually between  $10^6$  and  $10^4$  Hz.

## 2.9. FT-IR

FT-IR spectra were performed on a PerkinElmer spectrometer in the attenuated total reflection. Spectra were obtained by averaging 32 scans. The resolution was set to  $0.5 \text{ cm}^{-1}$ .



Scheme 1. PCIL synthesis.

### 2.10. DMA

Dynamic mechanical analysis (DMA) measurements were carried out with a TA Instruments DMA Q800 spectrometer working in the tensile mode. The strain magnitude was fixed at 0.01%. This value ensured that the tests were made in the linear viscoelastic domain. Measurements were performed in isochronal conditions (1 Hz) and the temperature was varied between  $-100$  and  $150$  °C at  $2$  °C  $\text{min}^{-1}$ .

## 3. Results and discussion

### 3.1. PCIL synthesis and chemical structure

The PCILs were obtained by an acid–base reaction of an amine with an organic acid (Scheme 1).

The structure of the starting acids and amines modulates PCIL properties. In this study, several acids with different acidities (pKa), structures, sizes, etc. were neutralized with triethylamine (Table 1). The pKa values of acids may be considered as an indication of how strongly a proton will be transferred from the acid to a base, though it must be noted that the pKa values that are usually considered for aqueous solutions [8,21] may not be appropriate for nonaqueous PCILs.

Except for the AA-TEA PCIL, all the ionic liquids synthesized (Table 1) resulted from a 1/1 mixture of acid and TEA. The stoichiometric mixture AA/TEA forms a biphasic solution, with the bottom phase containing 1.3 mol AA and 1 mol TEA and the upper phase being very rich in TEA. Even this 1.3AA/1TEA phase is not stable, since its distillation leads to a fraction of 3AA/1TEA. This behaviour was previously reported by Kohler et al. [22] who ascribed it to (i) the formation of a carboxylic acid cyclic dimer, (ii) the formation of a strongly polar 1:1 complex between carboxylic acid and amine, and (iii) a strong attractive interaction between this polar complex and the easily distortable ring (containing two hydrogen bonds) of the cyclic dimer. In terms of the conductivity and thermal stability of different AA/TEA mixtures ranging between 3/1 and 1/1, the AA/TEA = 3/1 exhibited the best results [23]. In the discussion that follows, AA/TEA 3/1 will be compared with the other PCILs. Like AA-TEA, TFA-TEA was purified by distillation while the other PCILs, which do not distillate, were dried for 48 h at  $130$  °C under vacuum, with no evaporation or degradation being observed.

### 3.2. PCIL thermal behaviour

The thermal properties of PCILs obtained from the different acids are shown in Table 1. All the modulated DSC analyses, performed at a scanning rate of  $5$  °C  $\text{min}^{-1}$ , exhibited an endothermic peak,  $T_m$ , and an exothermic peak,  $T_c$ , related respectively to the melting and crystallization of the PCILs. Unfortunately, due to their relatively rapid crystallization rate, it was generally difficult to measure  $T_g$  at this scanning rate. As shown in Table 1, the  $T_m$  of PCILs depends on the starting acid. Thus, the  $T_m$  of carboxylates are lower than those of sulfonates. The increase in the perfluorinated anionic chain length (PFBU-TEA, PFOC-TEA) leads to an increase in the hydrophobic character of the PCIL, which can be an asset since the elution of PCIL by the water produced by PEMFC can be avoided, or at least limited.  $T_m$  increases, however, with increases in the length of the perfluorinated anionic chain. The PCILs based on methanesulfonate exhibited similar  $T_m$  to that of TF-TEA. The difference between melting and crystallization points is more than  $40$  °C in the case

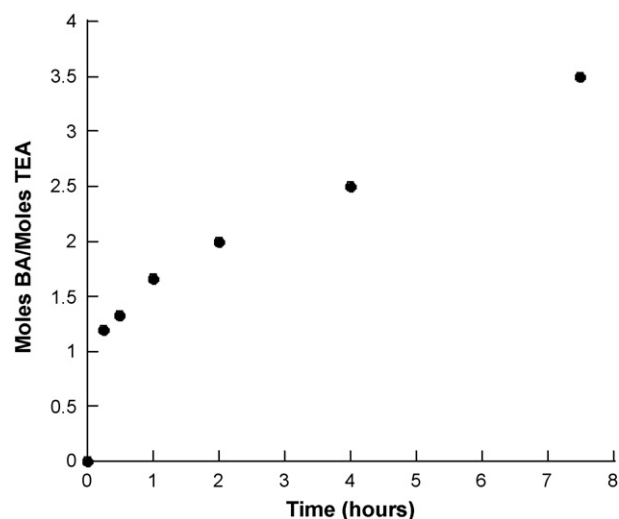


Fig. 2. Variation of BA/TEA ratio determined by  $^1\text{H}$  NMR from BA-TEA heated at  $150$  °C under flow air.

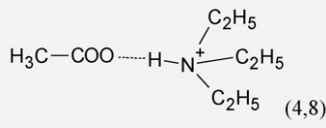
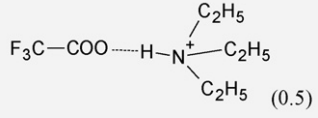
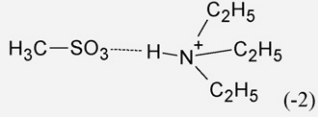
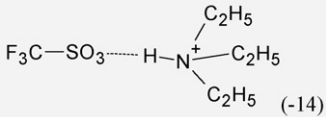
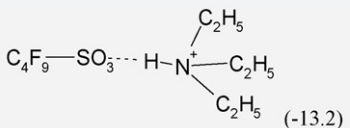
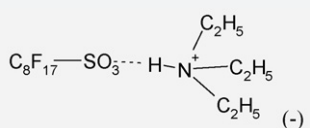
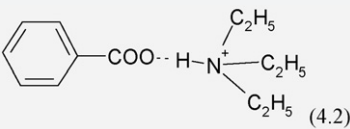
of MS-TEA, TF-TEA and TFA-TEA, while in the case of longer perfluorinated chains and aromatic rings this difference is less than  $15$  °C.

The thermogravimetric data show that weight loss temperature is strongly dependent on the strength of the starting acid. Thus, weight loss temperature,  $T_d$  (5% weight loss), was found to be lower than  $202$  °C for PCILs synthesized from the weaker acids, around  $300$  °C for PCILs synthesized from strong acids, and higher than  $370$  °C for those synthesized from superacids. The weight loss at much lower temperatures for the PCILs obtained from weak acids can be explained either by the deprotonation of ammonium, thus resulting in the initial volatile acid and amine, or by the chemical degradation of PCIL.

In the literature, it has been reported that PCILs obtained from weak acids are easily distillable. The mechanism involves the simple proton transfer from the cation back to the anion to reform the neutral species, i.e. original acid and base. After condensation, the PCIL is formed again [24]. This behaviour can be explained when the boiling points of the starting acid and amine are close (AA-TEA, TFA-TEA), which might clarify why, in the TGA experimental conditions, the weight loss for these two PCILs takes place in one step (only one peak is observed in derivative curves of TG). But, in order to discriminate between weight loss due to ammonium deprotonation and PCIL chemical degradation in the case of PCIL obtained from weak acid, the BA-TEA was synthesized and its degradation kinetic was observed by  $^1\text{H}$  NMR analysis. The difference between the boiling point of BA and TEA is greater than  $100$  °C.  $^1\text{H}$  NMR analysis is used to examine the structure of the non-evaporated product and to identify if weight loss is due to amine evaporation or other chemical degradation. The BA-TEA was heated to  $150$  °C (temperature lower than BA-TEA  $T_d$  but higher than TEA  $T_b$ ) under air flow and its evolution followed by conducting  $^1\text{H}$  NMR analysis at different time intervals. Following careful spectra analysis, it was concluded that weight loss is due mostly to TEA evaporation. Fig. 2 shows the evolution of ratios between BA and TEA calculated from  $^1\text{H}$  NMR spectra at different times. In NMR spectra any other new peaks were than those corresponding to BA-TEA and BA were observed. This proves that, for PCIL obtained from BA (weak acids), weight loss starts with ammonium deprotonation and evaporation of volatile TEA.

Based on these thermal results, it is clear that the use of weak acids for the synthesis of PCILs dedicated to high-temperature PEMFCs is not recommended, because at high temperatures the equilibrium shifts towards the formation of neutral starting prod-

**Table 1**  
Thermal characteristics of PCILs. Influence of the anion nature.

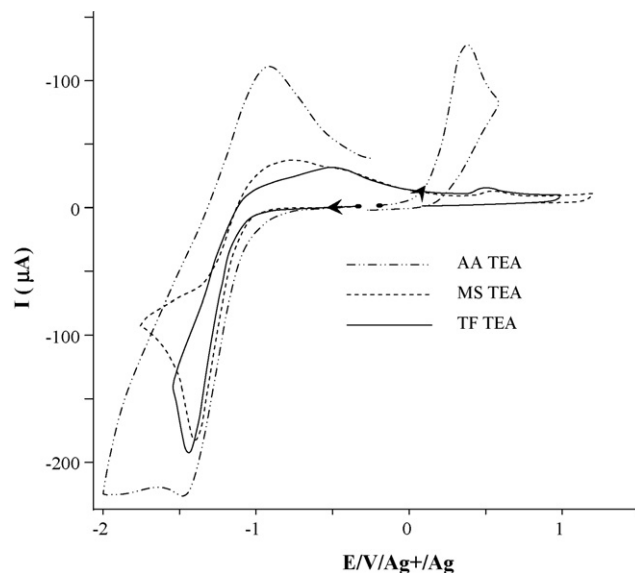
PCIL structure (pKa starting acids) [25]	Code	$T_m$ (°C)	$T_c$ (°C)	$T_g$ (°C)	$T_d^a$ (°C)
 (4,8)	AA-TEA	–	–	–	112 ( $T_b$ ) <sup>b</sup>
 (0.5)	TFA-TEA	2	–42	–83	190 ( $T_b$ ) <sup>b</sup>
 (-2)	MS-TEA	33	–24	–	305
 (-14)	TF-TEA	32	–20	–58	376
 (-13.2)	PFBu-TEA	61	50	–	383
 (-)	PFOc-TEA	82	71	–48	390
 (4.2)	BA-TEA	62	30	–	202

<sup>a</sup> 5% weight loss.<sup>b</sup> Boiling point.

ucts (amine and acid) and the evaporation of the more volatile ones [23].

### 3.3. PCIL electrochemical stability

Cyclic voltammetry of the PCIL was performed both in  $\text{CH}_3\text{CN} + 0.1 \text{ M}$  tetra *n*-butylammonium perchlorate electrolyte and in pure ionic liquid. Under both sets of conditions, similar electrochemical behaviour was observed. Concerning the cathodic process, for TF-TEA, MS-TEA, TFA-TEA, PFBu-TEA, and PFOc-TEA, no oxidation was observed up to +1 V vs.  $\text{Ag}/\text{Ag}^+$ , showing that no free triethyl amine contaminates the PCILs (Fig. 3). In the cathodic part, at close to  $-1.45 \text{ V}$  vs.  $\text{Ag}/\text{Ag}^+$ , reduction of the acidic triethylammonium moieties was detected. It should be noted that the shape and reversibility of this redox system depend strongly on the nature of the PCIL. High  $\Delta E_p$  values for the  $\text{H}^+/\text{H}_2$  system are measured, reaching up to 0.85 V in the case of TF-TEA. These strong distortions are presumably due to strong adsorption phenomena coupled with electron transfer. Based on a comparison of the CV of MS-TEA and TF-TEA (Fig. 2) ( $\Delta E_p = 0.65 \text{ V}$  for MS-TEA), this adsorption process must involve the generated amine produced during the reduction step and the anion of the PCIL.



**Fig. 3.** Cyclic voltammetry of PCILs on platinum electrode (diam. 3 mm) of 8 mM PCIL solution, in  $\text{CH}_3\text{CN} + 0.1 \text{ TBAP}$ ,  $\nu = 100 \text{ mV s}^{-1}$ .

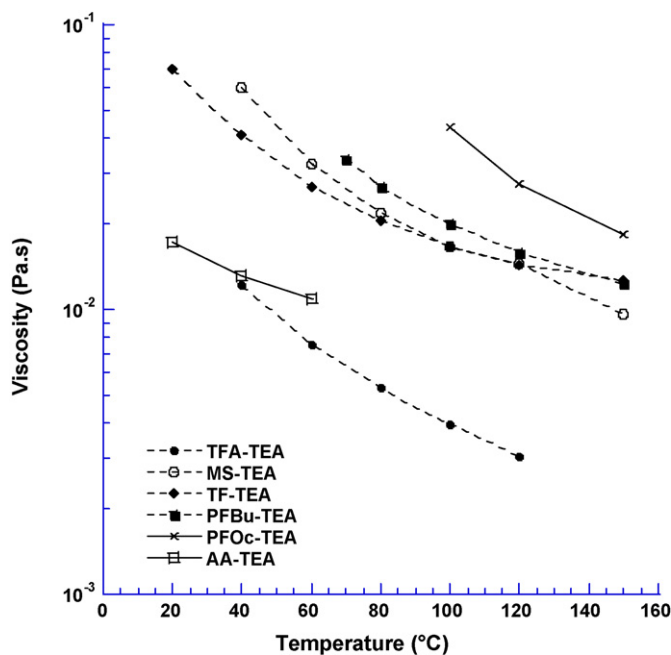


Fig. 4. PCIL viscosity dependency on temperature.

In addition, it should be noted that on the reverse scan, at 0.47 V, a signal characteristic of the oxidation of the triethylamine formed during the reduction process is observed.

In the case of AA-TEA, the CV is slightly different since the irreversible oxidation of the acetate anion is observed at 0.65 V, whereas the reduction shows the superimposition of acetic acid and ammonium whose reduction potentials are relatively close. For AA-TEA, if we take into account the fact that the ammonium salt and associated acetic acid present very low acidity, the two reduction processes are relatively close.

#### 3.4. PCIL viscosity

As conductivity depends on ionic mobility, which in turn is dependent on viscosity, a rheological analysis is indispensable in order to assess the influence of viscosity on conductivity.

First we checked that the different PCILs exhibit Newtonian behaviour, i.e. their viscosity, at a given temperature, is independent of the applied shear rates. The comparative plots of viscosity vs. temperature are shown in Fig. 4.

The viscosity of all PCILs decreases as temperature increases. The explored temperature range differs according to the ionic liquid as the measurements were only performed above the melting point of the PCIL. It may be noted, however, that TFA-TEA and AA-TEA exhibit very low viscosity ranging from  $10^{-2}$  to  $4 \times 10^{-3}$  Pa.s, while for the other PCILs, viscosity ranges from  $10^{-1}$  to  $10^{-2}$  Pa.s. Viscosities are similar for MS-TEA and TF-TEA. For the PCILs containing perfluorinated sulfonate anions, viscosity increases with increasing anion chain length. However, a significant difference was observed between PFBu-TEA and PFOc-TEA.

Viscosity is dependent on ion–ion interactions, Van der Waals interactions and hydrogen bonding (with greater interaction leading to higher viscosities), but also on molecular weight. The distinctly low viscosity of TFA-TEA as compared to MS-TEA and TF-TEA cannot be related to a difference in molecular weights, which are 216, 198 and  $252 \text{ g mol}^{-1}$ , respectively. This difference in viscosity could be related to the intermolecular interactions or the dissociation degree, which should be higher for the sulfonates than for the carboxylate. Indeed, both previous sulfonates

are weaker bases than the TFA carboxylate, thus favouring ion–pair dissociation, hence stronger ion–ion interactions. Nevertheless, PFBu-TEA exhibited viscosities only slightly higher than those obtained for MS-TEA and TF-TEA, in agreement with data from the literature [25]. The dissociation degree of TF-TEA and PFBu-TEA should be similar as both salts originate from superacids whose Hammett–Deyrup acidity functions, respectively  $-14.1$  and  $-13.2$  at  $22^\circ\text{C}$ , are very close [26]. But the molecular weight of PFBu-TEA ( $402 \text{ g mol}^{-1}$ ) is 60% higher than that of TF-TEA and twice that of MS-TEA. Consequently, the dilution of ionic functions by a longer perfluorinated chain induces a decrease in ion–ion interactions. This loss in viscosity, due to a decrease in ion–ion interactions, should partly counterbalance the increase in viscosity related to the increase in molecular weight. The dilution of ions by a long perfluorinated chain should, however, have an impact on the dissociation degree. The increase in the length of perfluorinated chain from 4 to 8 carbon atoms, however, increases viscosity by a factor of 2.

#### 3.5. PCIL conductivities

The Arrhenius plots of aliphatic PCILs are compared in Fig. 5 for a temperature domain of  $20$ – $150^\circ\text{C}$ . The PCILs were melted before their transfer to the conductivity cell. Hence, due to the substantial difference between  $T_m$  and  $T_c$  (Table 1), the solid–liquid phase transition in Arrhenius plots was observed only for PFBu-TEA and PFOc-TEA, the MS-TEA and TF-TEA remaining liquid even at  $20^\circ\text{C}$ .

Among the similar aliphatic anions, i.e. bearing only one carbon attached to the ionic function, TF-TEA exhibits the highest conductivities at high temperatures. It is, however, closely followed by the others, namely  $\text{MS-TEA} > \text{TFA-TEA} > \text{AA-TEA}$ . Obviously, in addition to its low thermal stability, the conductivity of AA-TEA that originates from several factors (carboxylic acid, carboxylate and ammonium) cannot be compared to other conductivities. Conductivities decrease significantly with the length of perfluorinated anionic chains. It is well known that conductivity depends on ionic mobility, related to viscosity, and on the concentration of mobile ions, related to salt concentration. In order to separate conductivity from the viscosity factor, conductivity was plotted against viscosity (Fig. 6a). This plot shows that, at the same viscosity, TF-TEA is the ionic liquid with the best conductivity, very closely followed by MS-TEA and then PFBu-TEA, while TFA-TEA is markedly less conductive. This behaviour should reflect a difference in the dissociation degree but due to (i) the different molecular weights and (ii) the dependence of conductivity on temperature (the same viscosities being obtained at different temperatures), it is difficult to accurately assess the dissociation gaps. In order to separate conduc-

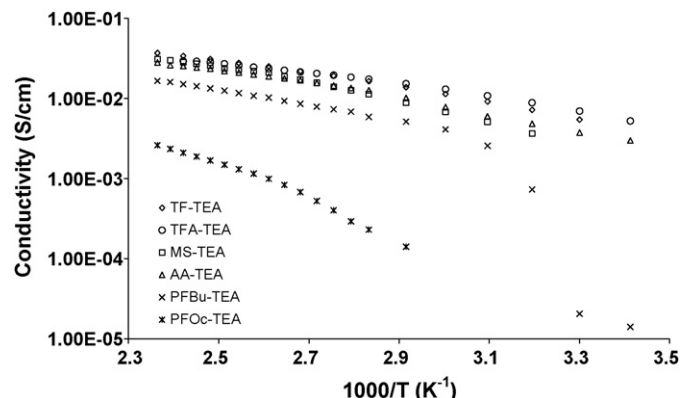


Fig. 5. PCIL conductivity Arrhenius plots.

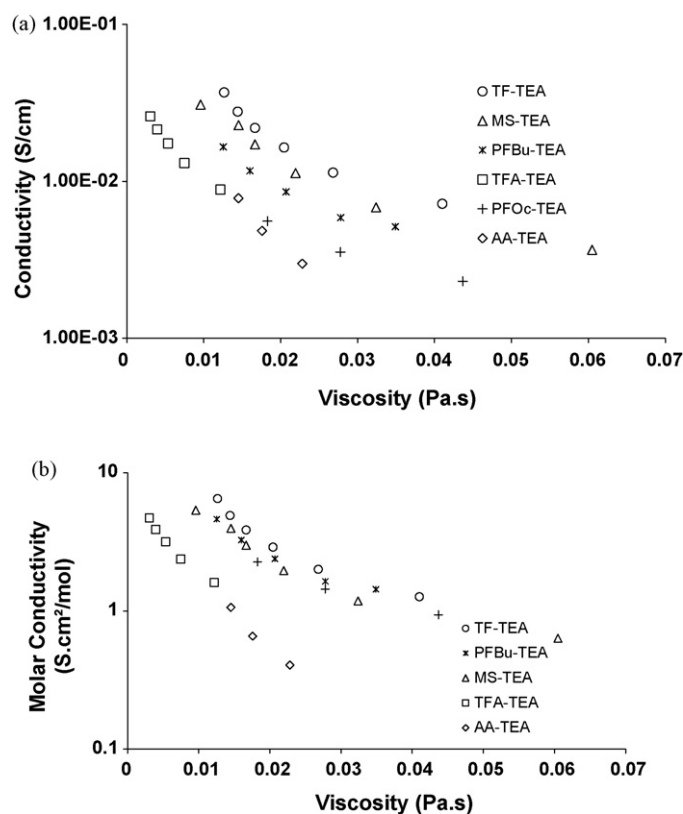


Fig. 6. (a) Conductivity vs. reciprocal temperature plots of different PCILs and (b) plots of molar conductivity vs. viscosity of different PCILs.

tivity from both viscosity and ionic liquid concentration, equivalent conductivity was plotted vs. viscosity. Determination of the equivalent conductivity assumes knowledge of ionic liquid density at each temperature, which allows the ionic liquid concentrations to be calculated. However, it is not easy to accurately determine densities at high temperatures.

Density obviously decreases following a temperature increase. This decrease remains, however, limited within the temperature range investigated. Thus from 25 to 50 °C, a linear thermal expansivity  $\alpha$  close to  $7 \times 10^{-4} \text{ °C}^{-1}$  was measured for MS-TEA, TF-TEA, AA-TEA and TFA-TEA.

In the case of PFBu-TEA, density was measured only at 50 °C before crystallization. The same thermal expansivity of  $7 \times 10^{-4} \text{ °C}^{-1}$  was used to calculate the density for PFBu-TEA at different temperatures. Unfortunately, for PFOc-TEA due to its high melting point, we did not succeed in obtaining an accurate value of its density. Thus its equivalent conductivity was not determined.

By inference from Fig. 6b, it can be considered that the PCILs based on sulfonate anions have, at the same viscosity, close dissociation degrees. TF-TEA is, however, more dissociated than both the other sulfonates.

Table 2  
Self-diffusion coefficients and cationic transference numbers ( $T^+$ ) of PCILs at 375 K.

PCIL (390 K)	$D_+$ (cm <sup>2</sup> s <sup>-1</sup> )	$D_{\text{TEA}}$ (cm <sup>2</sup> s <sup>-1</sup> )	$D_-$ (cm <sup>2</sup> s <sup>-1</sup> )	$T^+$ <sup>a</sup>	Viscosity (Pa s)
MS-TEA	$2.71 \times 10^{-6}$	$2.67 \times 10^{-6}$	$2.38 \times 10^{-6}$	0.53	0.0167
TF-TEA	$2.13 \times 10^{-6}$	$2.11 \times 10^{-6}$	$1.82 \times 10^{-6}$	0.54	0.0185
AA-TEA	$9.2 \times 10^{-6}$	$6.75 \times 10^{-6}$	$8.17 \times 10^{-6}$	0.53	0.0177
TFA-TEA	$7.0 \times 10^{-6}$	$7.02 \times 10^{-6}$	$6.45 \times 10^{-6}$	0.52	0.0045
PFBu-TEA	$1.14 \times 10^{-6}$	$1.13 \times 10^{-6}$	$8.43 \times 10^{-7}$	0.57	0.021
PFOc-TEA	$4.14 \times 10^{-7}$	$3.99 \times 10^{-7}$	$2.50 \times 10^{-7}$	0.62	0.042

<sup>a</sup> The cationic transference numbers  $T^+$  were calculated using equation:  $T^+ = D_+ / (D_+ + D_-)$ .

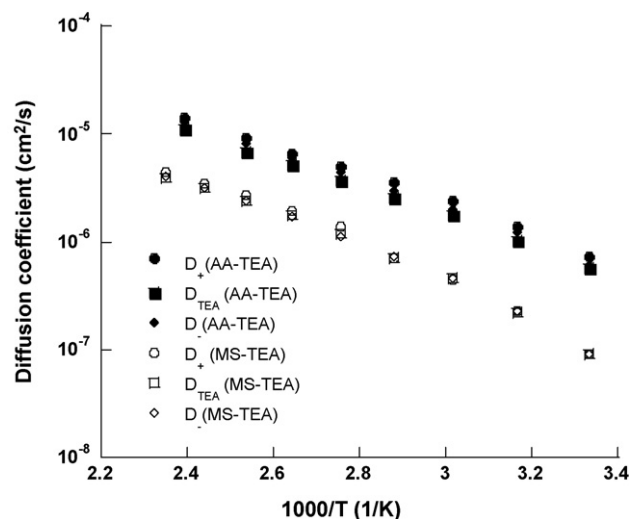


Fig. 7. Diffusion coefficients dependency on temperature for MS-TEA and AA-TEA.

### 3.6. PCIL diffusion coefficients and dissociation degree

PFM-NMR was used to examine the structure of these liquids through the measurement of a dynamic property on a macroscopic space scale of 1–100  $\mu\text{m}$ . Thus, self-diffusion coefficients of H<sup>+</sup> ( $D_+$ ), TEA ( $D_{\text{TEA}}$ ) and the anion ( $D_-$ ) in these different systems were measured by pulsed gradient NMR and their values measured at different temperatures ranging between 20 and 150 °C, and their values at 390 K are shown in Table 2.

The dependence of diffusion coefficients on temperature exhibits a VTF behaviour (Fig. 7).

The self-diffusion coefficients of these different species in PCIL provide valuable insights into the H<sup>+</sup> diffusion mechanism and the structure of the mobile species inside these ionic liquids.

From Table 2 and Fig. 7, and from previously reported results [18], three observations may be made about the H<sup>+</sup> diffusion mechanism: (i) the diffusion coefficients of three species (H<sup>+</sup>, anion, amine) are different in PCILs originating from a weak acid AA, leading to the assumption of H<sup>+</sup> diffusion by the Grotthus mechanism; (ii) similar diffusion coefficients are measured for TFA-TEA, allowing the predominance of ion-pair association to be assumed; and (iii) the diffusion coefficients of H<sup>+</sup> and the amine are similar but higher than that of the anion, in agreement with the assumption of a proton being transported by the ammonium via a vehicular mechanism. Generally, for the PCIL that proved a good thermal stability (obtained from a strong or a super acid) the proton are transported by the ammonium via a vehicular mechanism.

A good correlation between self-diffusion coefficients and viscosities was observed. The cationic transference numbers range between 0.5 and 0.62. The lowest value, in agreement with the previous results on conductivity vs. viscosity, corresponds to TFA-TEA, the highest one being obtained, as expected, for the longest perfluorinated chain.

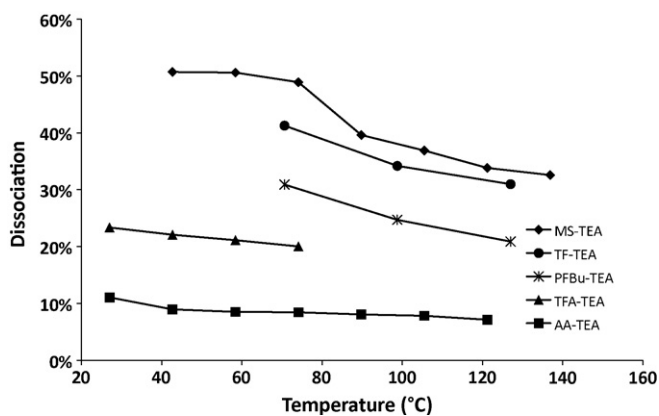


Fig. 8. Dissociation rate vs. temperature of different PCILs.

Even if the diffusion coefficients of the different species examined fall within the same range, their relative values reveal striking differences.

The diffusion coefficients determined by PFG-NMR concern not only free ions but also neutral ion pairs and aggregates. For free ions and solvent-separated ion pairs, the Nernst–Einstein equation may be used to forecast ionic conductivity,  $\sigma_{\text{calc}}$ , from the diffusion coefficients of the cation and anion. This approach was already used in the previous paper of Iojoiu et al. [16].

$$\sigma_{\text{calc}} = \frac{F^2[D_+ + D_-]}{RT}$$

The Nernst–Einstein equation only allows the order of magnitude of the dissociation to be determined, and in our case allows comparing PCIL dissociation. Indeed, this relationship is commonly considered as valid for the infinitely dilute state, where all the ion pairs are assumed to be dissociated. Using diffusion coefficients obtained by NMR leads to overestimation of conductivity, since neutral species, i.e. ion pairs, diffuse but do not contribute to conductivity.

From the  $\sigma_{\text{exp}}/\sigma_{\text{calc}}$  ratios plotted vs. temperature in Fig. 8, the highest dissociation degree can be ascribed to MS-TEA, closely followed by TF-TEA. A greater gap is observed between TF-TEA and PFBu-TEA and then with the carboxylates. The significant gap between TFA-TEA and TF-TEA is in agreement with previous results concerning diffusion coefficients and the plots of equivalent conductivity vs. viscosity which show mostly ion-pair association in the case of TFA-TEA. AA-TEA gives the lowest dissociation rate. The behaviour of PFBu-TEA is intriguing as, despite viscosity and anion nucleophilicity close to those of TF-TEA, its dissociation degree drops by a factor of 1.4. It might be assumed that the dilution of

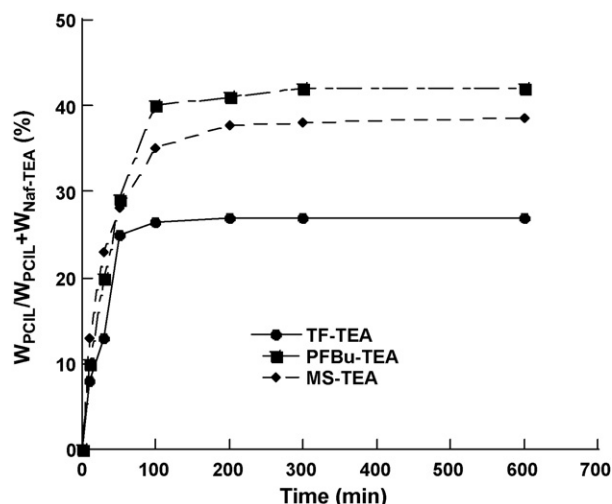


Fig. 9. Neutralized Nafion PCIL uptake at 80°C.

the ionic species by apolar perfluorobutyl moieties decreases ion-pair dissociation or favours ion micelle formation. For all the PCILs, a slight decrease in dissociation degree was observed with increases in temperature.

### 3.7. Blending neutralized Nafion with PCILs

If PCILs were blended with Nafion, without any neutralization of the Nafion acidic functions, an exchange would occur between the Nafion protons and the ammoniums of the PCILs, thus releasing molecular acids. To avoid such a release we first neutralized the Nafion acidic functions with the same amine as used in PCIL, i.e. TEA. The modified Nafion (Naf-TEA) was then swollen by the appropriate PCIL.

#### 3.7.1. Membrane synthesis: impact of PCIL structure on neutralized PCIL uptake

PCIL uptake, expressed in weight %, ionic exchange capacity (IEC) and mol PCIL/mol  $\text{SO}_3^-$  ratios of Nafion are shown in Table 3. Due to their instability at high temperatures, the PCILs derived from carboxylic acids were not blended with neutralized Nafion. Swelling was very fast in the first hours and then reached a plateau, depending on the PCIL used (Fig. 9). Membrane stability was checked by keeping membranes at room temperature outside the PCIL. Thus for the more swollen membranes (Table 3), PCIL release was less than 2% in the first 2 days and than their weights remained constant.

Table 3  
PCIL uptakes at 80°C.

PCIL	% PCIL <sup>a</sup>		IEC <sup>b</sup> (x PCIL + y $\text{SO}_3^-$ Naf-TEA) (mol H <sup>+</sup> kg)	mol <sub>PCIL</sub> /mol( $\text{SO}_3^-$ of Naf-TEA)
	Initial <sup>c</sup>	Final <sup>d</sup>		
TF-TEA	28	27	1.68	1.78
MS-TEA	38.5 (19) <sup>e</sup> (25) <sup>f</sup>	19 25	2.4 (1.63) (1.89)	3.59 (1.43) (2.04)
PFBu-TEA	42	40	1.49	2
PFOc-TEA	Solvent			

<sup>a</sup> %PCIL =  $((w_f - w_i)/w_f) \times 100$  where,  $w_f$ : membrane weight after swelling,  $w_i$ : membrane weight before swelling.

<sup>b</sup>  $\text{IEC}_{\text{electrolyte}} = \frac{\% \text{PCIL}}{100} \times \text{IEC}_{\text{PCIL}} + \frac{100 - \% \text{PCIL}}{100} \times \text{IEC}_{\text{Naf-TEA}}$ .

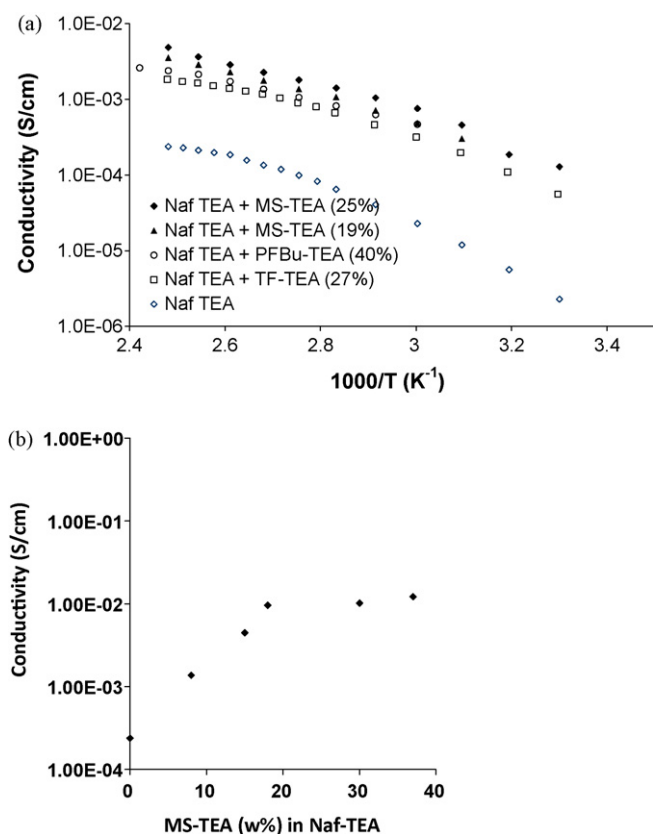
<sup>c</sup> PCIL uptake after immersing different times the Naf-TEA in corresponding PCIL.

<sup>d</sup> PCIL uptake after storage the swollen membrane a week outside of PCIL at room temperature.

<sup>e</sup> Membranes swollen during 1 h.

<sup>f</sup> Membranes swollen during 5 h.





**Fig. 10.** Membrane conductivities vs. temperature. (a) For similar PCIL uptake (Naf-TEA + MS-TEA (25%)); similar IEC (Naf-TEA + MS-TEA (19%), Naf-TEA + TF-TEA (27%)) similar moles PCIL/moles SO<sub>3</sub> of Nafion (Naf-TEA + MS-TEA (25%), Naf-TEA + PFBu-TEA (40%)). (b) Different MS-TEA concentrations in Nafion membrane.

For rather similar salts such as TF-TEA and MS-TEA, the swelling ratio of Naf-TEA is higher for non-fluorinated MS-TEA, even if higher uptake would be expected for TF-TEA due to its trifluoromethyl moiety. However, an increase in the length of the perfluorinated chain induced an increase in PCIL uptake, with PFOc-TEA able to fully dissolve the Naf-TEA. As the molecular weight of MS-TEA is lower than that of TF-TEA, the total IEC of the membrane is higher in Naf-TEA blended with MS-TEA (Table 3). For that, we compare the membrane conductivity not only on the same PCIL weigh uptake but also at the same IEC (Fig. 10).

### 3.8. Membrane conductivities

The Arrhenius trace compares the conductivities of neutralized Nafion with those of the blends (Fig. 10). Although the conductivities of pure modified Nafion are close to 0.2 mS cm<sup>-1</sup> (at 120 °C), they are markedly lower than those of membranes swollen with PCIL. Therefore, despite the non-negligible contribution of Naf-TEA in terms of ammonium concentration, the conductivity of the blends seems to significantly improve by adding even a small amount of PCIL. The surrounding of the dangling ionic functions of neutralized Nafion by PCIL should increase their conductivity contribution as compared to that measured in the membranes free of PCIL. Another advantage of these ionic functions is related to their cationic transference number, which should be close to 1. Thus, as the  $T^*$  of these PCILs range between 0.5 and 0.64, Naf-TEA should decrease the impact of a possible gradient in PCIL concentration occurring in the membrane during PEMFC operation.

Despite the fact that TF-TEA was found to have the best conductivity among pure PCILs, the blended ionomer incorporating MS-TEA exhibited much higher conductivities than that incorpo-

rating TF-TEA. This clearly demonstrates that the best PCIL does not result in the best blended ionomers and that the PCIL uptake, structure, interactions with the polymer, and structuring inside the membrane are also decisive parameters. This clear gap could obviously partly depend on the PCIL uptake by Naf-TEA. A comparison of the conductivities of MS-TEA and TF-TEA blends, at similar w% uptakes (25% vs. 27%) and IEC (1.63 vs. 1.68), shows, however, that the former is still more conductive.

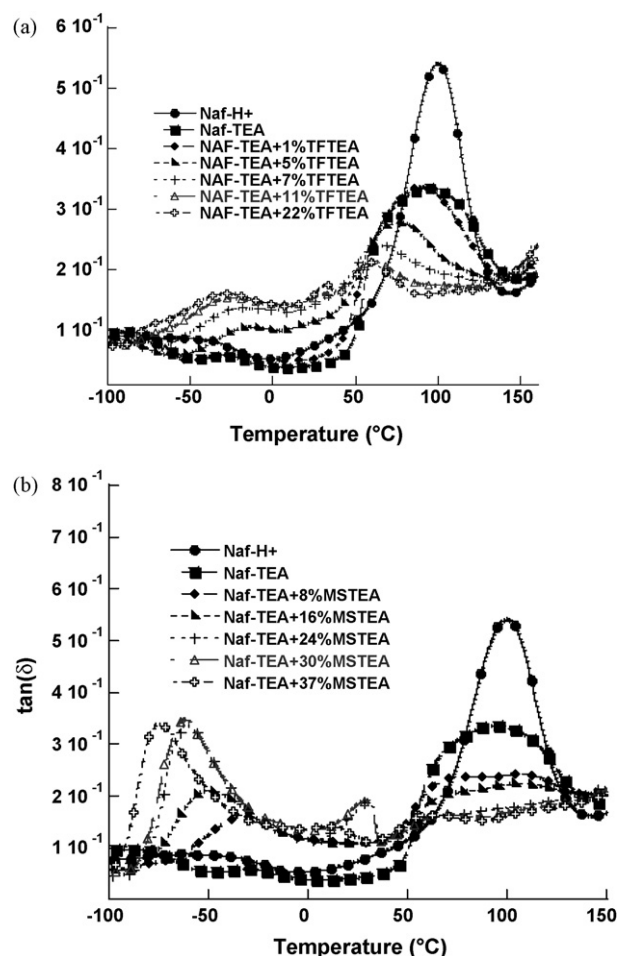
The Naf-TEA + PFBu-TEA membrane, despite (i) its lower IEC compared to that of the Naf-TEA + TF-TEA and (ii) the much lower conductivity of PFBu-TEA compared to TF-TEA, shows a higher conductivity. Taking into account perfluorobutyl size and the moles of PFBu-TEA/SO<sub>3</sub> of Naf-TEA (Table 3), better ionic percolation might be inferred.

A significant increase in Naf-TEA conductivity was observed even for very low MS-TEA concentrations in the membrane. Conductivity first increases very sharply with the increase in PCIL concentration, reaching a maximum that is specific to the nature of the PCIL. Once this maximum is reached, conductivity remains almost constant up to the maximum uptake PCIL concentration (Fig. 10b).

### 3.9. Membrane mechanical properties

The mechanical analyses were restricted to the blends involving MS-TEA, TF-TEA and neutralized Nafion.

The dependence on temperature of the loss tangent ( $\tan \delta$ ) and storage modulus ( $E'$ ) of the membranes, shown in Figs. 11 and 12



**Fig. 11.** Storage modulus vs. temperature (a) Naf-TEA + x%TF-TEA and (b) Naf-TEA + x%MS-TEA.

respectively, was measured by a dynamic oscillatory method with sinusoidal mechanical elongations of 30  $\mu\text{m}$  at 1 Hz (see Section 2). The analysis of  $\tan(\delta)$  (Fig. 11) shows that Nafion 117 exhibits, at ca. 102 °C and in accordance with other studies, a typical  $\alpha$ -relaxation event that was attributed to the motion of side chains in cluster aggregates. It should be observed that the  $\alpha$ -relaxation peak decreases in intensity and the maximum of peak temperature shifts ( $T_{\alpha}$ ) according to: (Naf-H+) 102 °C > (Naf-TEA) 92 °C > (Naf-TEA + TF-TEA)  $\approx$  (Naf-TEA + MS-TEA) 61–92 (according to PCIL uptake). Results reveal that the energy loss corresponding to the motion of side chains in cluster aggregates is: (a) higher in Nafion 117 where hydrogen bonds with strong dipole–dipole interactions are expected; (b) reduced in Naf-TEA, where weak Van der Waals interactions occur between ethyl terminated side groups, but with more steric hindrance interferences; (c) very low in Naf-TEA + PCIL where the sterically hindered neutralized side groups are solvated by PCIL. At 0 °C, the membranes exhibited storage moduli of 817, 518 and between 817 and 97 MPa respectively for Naf-TEA, Naf-H+ and different PCIL concentrations in Naf-TEA + PCIL blends (Fig. 12). For Naf-TEA + PCIL, the storage modulus decreases when PCIL concentration increases. These results indicate that an enhancement of  $E'$  with respect to Naf-H+ is obtained in Naf-TEA. This can be ascribed to the strong steric hindrance between neutralized side groups. In addition, in this latter sample, the value of  $T_{\alpha}$ , slightly lower than that of Naf-H+, suggests that the decrease in mechanical energy loss corresponds to an increase in the mobility of side groups. Finally, in Naf-TEA + PCIL blends, PCIL significantly affects the mechanical properties of neutralized Nafion by lowering

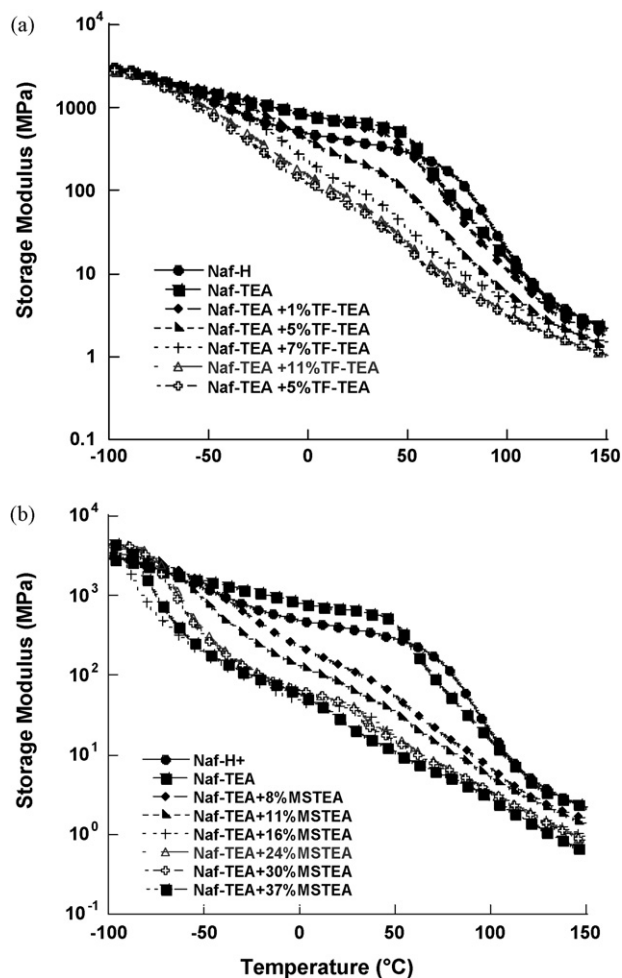


Fig. 12.  $\tan(\delta)$  vs. temperature (a) Naf-TEA + x%TF-TEA and (b) Naf-TEA + x%MS-TEA.

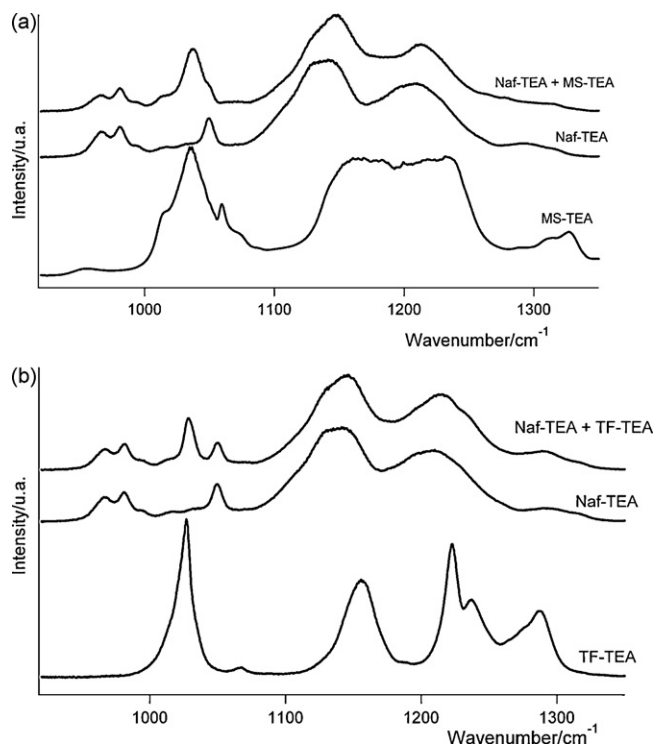


Fig. 13. FT-IR spectra of (a) MS-TEA, Naf-TEA, Naf-TEA + 37%MS-TEA and (b) TF-TEA, Naf-TEA, Naf-TEA + 25%TF-TEA.

the steric hindrances and increasing the plasticization of the host ionomeric matrix.

In contrast to Naf-H+, Naf-TEA and all the blends lead to distinct peaks with well-resolved  $\alpha$  and  $\beta$  relaxations. In addition, a significant increase in the relative intensity of the  $\beta$  relaxation is observed when PCIL content in the blend increases. This behaviour suggests that as PCIL concentration increases, larger populations of chains are capable of activated motion at lower temperatures, which can be attributed to a very weak interaction between side chains [27]. With the increase in PCIL content, taking into account the nano-phase separated morphology of the Nafion membrane, the formation of PCIL aggregates is, however, expected to occur in the ionic phase. In the  $\tan(\delta)$  DMA graphs new peaks are observed at around 30 °C for higher PCIL concentration. We suppose these peaks correspond to the PCIL aggregates melting. The peaks corresponding to  $\beta$  relaxation are wider and shift to lower temperatures as PCIL concentration increases. The  $T_{g}$ s of TF-TEA and MS-TEA being respectively  $-58$  and  $-73$  °C, the superposition of two (or more) relaxations, related to the PTFE chain and the PCIL aggregates, can be inferred.

Moreover, in the case of membranes based on MS-TEA the magnitude of  $\beta$  relaxation is much higher than that of membranes based on TF-TEA. It can be inferred that there is a better organisation of MS-TEA in Naf-TEA and higher mobility of the PTFE chain in this blend.

### 3.10. FT-IR analysis

Fig. 13 shows the absorption spectra in the window 900–1400  $\text{cm}^{-1}$  of pure PCIL (MS-TEA Fig. 13a; TF-TEA Fig. 13b), Naf-TEA and Naf-TEA + PCIL. Peaks can be observed associated with: (a) CF regions in the range 1130–1377  $\text{cm}^{-1}$  attributed to fluoro-carbon chain modes of PTFE-like domains of Nafion; (b) polyether side chain modes in the region 957–993  $\text{cm}^{-1}$ ; (c) the terminal sulfonic anion vibrations of Nafion at 1050  $\text{cm}^{-1}$ ; (d) the triflate or methanesulfonate anion vibrational modes,  $\text{CF}_3\text{SO}_3^-$  (S–O band at

1026  $\text{cm}^{-1}$ ) or  $\text{CH}_3\text{SO}_3^-$  (S–O band at 1035  $\text{cm}^{-1}$ ); (e) the tertiary ethyl amine cation vibrations,  $\text{Et}_3\text{N-H}^+$  [28–30]. A closer inspection of Naf-TEA-TEA + PCIL shows that the vibrational bands due to both PCIL (MS-TEA or TF-TEA) and Nafion-TEA are reproduced in the spectra of the Naf-TEA + PCIL membrane, which basically are the sum of two contributions.

A comparison of Naf-TEA and Naf-TEA + PCIL FT-IR spectra in the CF region reveals no significant changes in the shape of peaks (which would be indicative of fluorocarbon chain conformations), suggesting that the structure and composition of the hydrophobic domains of the Naf + PCIL are similar to those of pristine Naf-TEA. These results are in agreement with the studies of Martinelli et al., which reported that interactions between TFSI<sup>-</sup> ionic liquids and a PVdF matrix were absent or negligible [10].

Further insights into the interactions between the PCIL and polymer matrix of Naf-TEA were sought by carrying out a careful analysis of the vibrational modes of triflate anion, methanesulfonic anion and Nafion sulfonate anion, and in particular the  $\text{SO}_3$  band of Nafion (1050  $\text{cm}^{-1}$ ), S–O band of TF-TEA (1026  $\text{cm}^{-1}$ ) and S–O band of MS-TEA (1035  $\text{cm}^{-1}$ ). Comparison of Naf-TEA and Naf-TEA + MS-TEA in the 1000–1100  $\text{cm}^{-1}$  region indicates that no significant modification in the shape or in the vibration wave number is detected, thus suggesting that the confinement of MS-TEA in the Naf-TEA matrix does not alter the structure/organisation of the pristine MS-TEA. In the case of membranes Naf-TEA + TF-TEA, the TF-TEA S–O band shifts from 1226 to 1229  $\text{cm}^{-1}$ , which may indicate the presence of new interactions involving TF-TEA compared with pure ionic liquid that might explain the lower conductivity of membranes based Naf-TEA + TF-TEA.

#### 4. Conclusion

This study emphasizes the importance of PCIL uptake by the functional polymer, since the best PCIL does not necessarily result in the most conductive membrane. To optimize membrane conductivities, the ionic liquid must therefore be adapted so as to obtain the appropriate PCIL uptake and interaction with the host polymer. Emphasis was placed in this study on understanding the conduction mechanisms. Nonetheless, using modified Nafion as a host polymer resulted in conductivity exceeding 10  $\text{mS cm}^{-1}$  at 130 °C. This result is very encouraging as Nafion is present in the electrode active layers. These electrodes could therefore be used after blending Naf-TEA with an optimized PCIL in high-temperature PEMFCs. Lastly, the mechanical strength of Nafion-based membranes is, in our opinion, too low. New membranes hosting the same PCILs are already under study in our group (patents pending), and details will soon be published. They present slightly higher conductivities than those of the blended Nafion membranes, while exhibiting storage moduli exceeding 100 MPa up to at least 150 °C. This should allow very thin PCIL-based membranes to be produced.

#### Acknowledgments

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