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## Ionic Liquids and their hosting by polymers for HT-PEMFC membranes

Journal:	<i>Fuel Cells</i>
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Referee(s)' Comments to Author:

Reviewer: 1

Comments to the Author

The manuscript is interesting and well-written. Thus, I recommend its publication as is.

Reviewer: 2

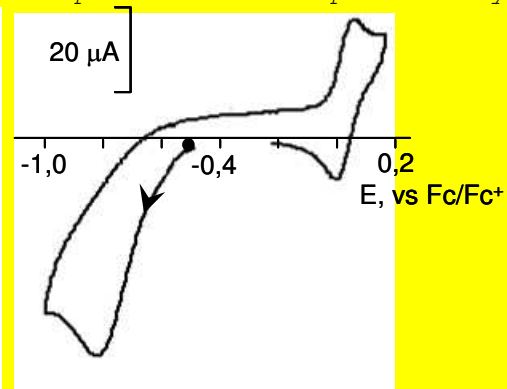
Comments to the Author

This manuscript describes properties of many protic ionic liquids as electrolyte for fuel cell. Overall, I feel a lack of comprehensive review and citation of the relating previous studies.

As this paper, which is not intended to be a review, includes already 31 references, we added only one reference that is a review dealing with the proton-conducting ionic liquids.

Although the authors aims at the applying these protic ionic liquids and their composite membranes to fuel cells, there are no data about fuel cell reactions (HOR and ORR) and also fuel cell performances. These are my major comments. I would conclude that this paper needs major revision by addressing these major comments and the following detailed comments.

We performed ORR investigation and we have available some data. In this topic a wide variety of Ionic Liquids has however been prepared and characterized by several academic laboratories. The purpose of this paper was, by selecting a limited number of ionic liquids, to get a better understanding of the relations between conductivity, transference numbers, viscosity, humidity that govern the performances of ionic liquids. In addition as the latter are liquids a particular attention has been paid to the ionic liquid/host polymer interactions that are essential as they govern the membrane performances. Therefore the selected approach was to focus on material science aspects (physical-chemistry, mechanic etc.) to validate whether such blends can meet the requirements to be operated at high temperature and in poorly humidified conditions (in terms of conductivity and thermomechanical performances). Thus, inclusion of our preliminary ORR tests, in this manuscript would be harmful to the homogeneity and the balance of the paper. [However I send to the reviewer the ORR result, which I repeat deals with preliminary results]



Cyclic voltammogram of  $O_2$  saturated TEATf on vitreous carbon disk electrode (3mm diameter), scan rate =  $100 \text{ mVs}^{-1}$ ,  $T = 50^\circ\text{C}$ . Internal redox reference: ferrocene

1. The properties of certain protic ionic liquids, which the authors report in this paper, have already reported in literatures. The authors should refer to these papers and also need to address the similarity or the difference of the data.

Some of the results were previously published by our group (some of them from 2006, ISPE-10 lecture) and the others by other groups. As the PCILs

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3 properties drastically depend on their purity, their water content, and the  
4 characterization techniques used, we selected, in order to get a more  
5 accurate comparison, to refer to data obtained in the same conditions.  
6  
7

8 2. The authors claim that a change in  $T_m$  of cyclic ammonium PCILs can be  
9 explained by their geometry and flexibility. However, cyclopentane shows  
10 much lower  $T_m$  than cyclohexane. Similarly, pyrrolidine shows much lower  $T_m$   
11 than piperidine. I would like to know the authors' opinion about the  
12 difference between PCIL and neutral molecules?"  
13

14 In cyclopentane the medium angle ( $108^\circ$ ) according to a planar structure  
15 leads, in cycloalkane serie, to the lowest Pitzer angle tension ( $-$   
16  $0.75^\circ$ ) while the medium angle in cyclohexane ( $120^\circ$ ) exceeds the tetrahedric  
17 angle ( $109^\circ.5$ ) leading with the same assumption to a Pitzer tension of  $\sim +$   
18  $5.5^\circ$ . But from calorimetric measurements cyclohexane appears as the most  
19 stable cycloalkane. To explain this discrepancy it was proposed that  
20 cyclopentane has several non-planar conformations and in particular the  
21 envelop one. The same explanation was provided for cyclohexane with a  
22 variety of conformations and the well-known chair-boat equilibrium. When  
23 the methylene group is changed into an ammonium the medium angle should  
24 change as well as the ring tension and therefore impact on the planarity  
25 deformation. The reviewer remark is excellent but honestly, despite these  
26 assumptions, we cannot provide, as we did not perform X-Ray investigation,  
27 sounder explanations.  
28

29 3. Was sulfonated poly(ether sulfone) synthesized? If so, the molecular  
30 characterization is required. If not, the supplier should be given.  
31

32 The reviewer is right. The sulfonation process and characterisation of  
33 sulfonated polysulfones were already reported in references [23,24]. In  
34 experimental part we therefore include these references.  
35

36 4. Is the unit of Y axis in Figure 8 correct?  
37

38 Many thanks to the reviewer: we did a big mistake (factor  $10^6!!$ ). It has  
39 been corrected  
40

41 5. There are many typographical errors.

42 Grotthus >>> Grotthuss

43 It was modified

44 Bronsted >>> Brønsted  
45

46 It was modified  
47

48 trifluoromethylsulfonic acid >>> trifluoromethanesulfonic acid (page 10  
49 line 14)

50 voltametry >>> voltammetry (page 17 line 13)

51 They have been modified  
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## Ionic Liquids and their hosting by polymers for HT-PEMFC membranes.

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### Abstract:

The paper deals with proton-conducting ionic liquids (PCILs) for use, in combination with functional polymers, in membranes operating in High Temperature PEMFC. Monoammoniums derived from monoamines and half-neutralized diamines were investigated in the form of triflates. Promising results were obtained with the half-neutralized diamine-based PCIL, its conduction being governed by both Grotthuss-like and vehicular mechanisms, the respective contributions of which depend on temperature. In addition, their blending with Nafion results in a distinct reinforcement of the membrane.

**Keywords:** Fuel cells, Proton-conducting Ionic Liquids, membranes, PFG-NMR.

## 1. Introduction

Along with ensuring the availability of sufficient drinking water and food resources, finding new energy sources to provide alternatives to current sources based on fossil fuels is perhaps one of the main scientific and technological challenges facing human society in the present century. Indeed, in addition to the scarcity of oil resources, albeit temporarily alleviated by recent discoveries, pollution concerns make it indispensable to seek alternative energies e.g. photovoltaic and wind turbines, both requiring electrochemical storage sources to smooth the peaks in electricity production. Not only must the production of greenhouse gases, such as the renowned CO<sub>2</sub>, be drastically decreased but so too must emissions of a variety of chemical pollutants by gasoline- and diesel-powered internal combustion engines. In addition to their role in smoothing electricity production by solar plants and wind turbines (batteries, supercapacitors), advanced electrochemical energy sources can increasingly be used by themselves in automotive and electricity implementations.

Heat electricity cogeneration and tri-generation can be achieved using Fuel Cells, namely SOFCs (Solid Oxide Fuel Cells) or PEMFCs (Proton Exchange membrane Fuel Cells). Although the SOFC has a high operating temperature, which is an asset for this implementation, the PEMFC is also considered. Heat recovery will nevertheless be markedly improved by increasing the operating temperature of PEMFCs, currently around 80°C. The reliability target of PEMFC units dedicated to stationary applications was 20,000 hours in 2005 and it is planned to increase this to 90,000 hours by 2020. The cost per kW should decrease from 2005 to 2020 by a factor of 20! Both reliability and cost targets are stiff challenges.

The other promising implementation of electrochemical sources concerns automobiles. Moving from cars powered by gasoline and diesel internal combustion engines to electric EV and hybrid HEV & PHEV cars would make a significant contribution to decreasing urban

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3 pollution. While current hybrid cars like the Toyota Prius are partly powered by Nickel-Metal  
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5 Hydride batteries, car manufacturers are looking for more efficient energy sources. There are  
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7 two main options, lithium batteries and PEMFCs. Lithium batteries, thanks to their higher  
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9 energy and power densities, appear attractive provided that they meet the implementation  
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11 requirements in terms of both safety and cost per kWh. The other option, using PEMFCs,  
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13 needs to find a solution to the recharge time issue. A third option involves hybridizing lithium  
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15 batteries and PEMFCs. Indeed, Nissan and PSA have already built EV prototypes associating  
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17 lithium-ion batteries and PEMFCs. Once again, an increase in the operating temperature of  
18  
19 PEMFCs from 80° to at least 120°C would suit most car manufacturers as it would help  
20  
21 overcome one of the main issues relating to heat management in EV. Indeed, the electrical  
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23 yield of PEFMC is close to 50% and removal of the heat produced cannot be achieved with  
24  
25 current car radiators, at least in small to medium cars. In addition, increasing the operating  
26  
27 temperature will benefit PEMFCs as it will increase the tolerance of electrocatalysts to carbon  
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29 monoxide poisoning. Increasing the operating temperature of PEMFCs to 120°C requires that  
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31 high proton conductivities be maintained.  
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39 Membrane conductivities are mainly governed by their water uptake. Given that the  
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41 solution of pressurizing PEMFCs is generally excluded, current membranes must be replaced  
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43 by new membranes exhibiting high proton conductivities at the anhydrous state. The  
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45 composite approach involving the filling of ionomers with inorganic fillers that exhibit  
46  
47 intrinsic high proton conductivity, such as phosphatoantimonic acids, improves the  
48  
49 conductivities of various ionomers, in particular above 80°C, but it is unsuitable for  
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51 operations at  $T \geq 120^\circ\text{C}$  [1,2]. Another approach deals with the use of polymer-acid  
52  
53 complexes. Although anhydrous complexes between poly(oxyethylene) and phosphoric acid  
54  
55 allow reaching conductivities  $\geq 1$  mS/cm around 80°C, they would be unstable in a PEMFC  
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57 [3]. Other complexes obtained from poly( $\gamma$  aminopropylsiloxane), partly neutralized by triflic  
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3 acids, reached conductivities as high as 10 mS/cm at 120°C, [4] but once again the chemical  
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5 stability of the host polymer, in a PEMFC, seems questionable.  
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Complexes based on high-performance thermostable polymers could overcome the chemical issues related to the previous polymer complexes. Thus polybenzimidazole **PBI**, blended to phosphoric acid  $\text{H}_3\text{PO}_4$  has been proposed as a promising membrane for High Temperature PEMFCs [5,6] (HT-PEMFC). The monomer repeat unit of PBI is a fairly weak Lewis base that favours interaction with the acidic proton of phosphoric acid. The decisive parameter for obtaining highly conductive PBI/ $\text{H}_3\text{PO}_4$  membranes is the phosphoric acid uptake [6]. An increase in  $\text{H}_3\text{PO}_4$  doping levels results in a clear increase in membrane conductivity related to the increase in proton “carriers”. Thus at 150°C, for  $\text{H}_3\text{PO}_4$  doping levels of molarities 4.7, 6.7 and 14.5, respective conductivities of 18, 22 and 79 mS  $\text{cm}^{-1}$  were obtained. The huge acid excess, however, results in dramatic degradation in both the membrane (mechanical properties) and the electrodes [7]. A clear performance degradation [7] was reported after a lifespan test of ~550 h (500 h continuous operation and 50 h intermittent), performed in dry conditions, at 150°C, on a  $\text{H}_3\text{PO}_4$ /PBI-based PEMFC. Despite their drawbacks,  $\text{H}_3\text{PO}_4$ /PBI membranes have given rise to a worldwide research effort that should lead to an improvement in performance and lifespan, making PBI-based membranes one of the most relevant routes to achieving High Temperature PEMFC.

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An attractive alternative to phosphoric acid involves using proton-conducting ionic liquids (PCILs). Previous studies carried out, in particular by the laboratories of M. Watanabe [8-12] and A. Angell [13-15], have emphasized the high potential of these organic ionic liquids. Many data were published on PCIL, most of them been gathered in the review of Greaves et al. [16]. Nevertheless, these liquid salts must be embedded in a polymer to meet the requirements of PEMFC membranes in terms of thickness and safety. This contribution aims, through a multidisciplinary approach, to provide an overview of the impact of the



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3 structure of PCILs on their thermal, electrochemical and conductive behaviour. Special  
4 attention has been paid to membrane performance and, in particular, to the relationship  
5 between conductivity and mechanical stability. Although a huge variety of PCILs can be  
6 envisaged by combining various anions and ammoniums, this paper does not intend to be  
7 exhaustive. We have therefore decided to keep the same anion, i.e. triflate, and to vary the  
8 ammoniums.  
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## 20 **2. Experimental part**

### 21 Proton-conducting ionic liquid (PCIL) syntheses

22 The PCIL syntheses were performed following the protocol described in previous publication  
23 [17-21].  
24

25 PCIL water content was checked by Karl Fisher measurements and for all PCILs it was lower  
26 than 50 ppm.  
27  
28

29 PCIL purity was then checked by NMR, using a Bruker WM 250 spectrometer operating at  
30 frequencies of 250 MHz for the  $^1\text{H}$  and 235.3 MHz for  $^{19}\text{F}$ . The samples were dissolved in  
31  $\text{CDCl}_3$ . Peak assignments of PCILs were carried out by reference to the starting amines and  
32 acids.  
33

### 34 Cyclic voltammetry

35 All electrochemical measurements were made under an argon atmosphere in a dry glove box.  
36 Cyclic voltammetry (CV) experiments were performed using an Autolab potentiostat/  
37 galvanostat in  $\text{CH}_3\text{CN} + 0.1\text{M Bu}_4\text{NClO}_4$  (TBAP). The standard three-electrode  
38 electrochemical cell was used. The reference electrode was Ag wire/0.01 M  $\text{AgNO}_3$  in  $\text{CH}_3\text{CN}$   
39 0.1 M  $\text{Bu}_4\text{NClO}_4$ . Potentials can be converted to the SHE (Standard Hydrogen Electrode)  
40 system by adding 0.548 V [22]. The working electrode (5 mm in diameter) was a platinum disk  
41 polished with 2  $\mu\text{m}$  diamond paste (Mecaprex Presi). Thanks to this protocol, it was possible to  
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3 compare, at room temperature ( $\sim 30^\circ\text{C}$ ), the electrochemical behavior of the all PCILs. Cyclic  
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5 voltammetry allowed  $E_{pa}$  (anodic peak potential),  $E_{pc}$  (cathodic peak potential) and for  
6  
7 reversible processes  $E_{1/2}$  ( $= (E_{pa}+E_{pc})/2$ ) and  $\Delta E_p$  ( $=E_{pa}-E_{pc}$ ) to be determined. Some  
8  
9 experiments were however performed in pure ionic liquid (for PCIL's exhibiting melting  
10  
11 points fairly low). In that case, the  $\text{Ag}^+/\text{Ag}$  reference electrode was separated from the PCIL by  
12  
13 an intermediary compartment containing the same PCIL. This device was checked using  
14  
15 ferrocene ( $E_{1/2} = 0.09\text{V}/\text{Ag}^+/\text{Ag}$ ). It should be added that, both methods (pure PCIL or  $\text{CH}_3\text{CN}$   
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17 solution), led to close electrochemical behavior of the PCIL.  
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### 25 Thermal analysis

26  
27 Glass transition temperatures,  $T_g$ , melting temperatures,  $T_m$ , and crystallization temperature,  
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29  $T_c$ , were measured in nitrogen flow using a TA Instruments DSC 2920 modulated DSC.  
30  
31 Around 10 mg of the sample was placed in a DSC aluminium crucible in a glove box. In a  
32  
33 typical procedure, the samples were cooled rapidly to  $-100^\circ\text{C}$  and then heated at a rate of  
34  
35  $5^\circ\text{C}\cdot\text{min}^{-1}$  up to  $200^\circ\text{C}$ . The oscillation period was 60 s and its amplitude was  $\pm 0.6^\circ\text{C}$ .  $T_g$ ,  $T_m$   
36  
37 and  $T_c$  were taken as the inflection points of the increment of specific heat at respectively the  
38  
39 glass-rubber transition and the onset of the melting or crystallization peak.  
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43 Thermogravimetric measurements (TGA) were carried out using a Netzsch STA409 thermal  
44  
45 analyzer. Around 50 mg of the sample was heated from room temperature up to  $400^\circ\text{C}$  at  
46  
47  $10^\circ\text{C}\cdot\text{min}^{-1}$  in an air flow. The degradation temperature,  $T_d$ , corresponds to a 5% weight loss.  
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### 53 Rheometry

54  
55 Rheometrical measurements were performed using a TA ARG2 rotational rheometer.  
56  
57 Viscosity was determined through controlled shear measurements using both parallel plates  
58  
59 and cone and plate geometry. Viscosity measurement under shearing involves imposing a  
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3 shear rate  $\dot{\gamma}$  ( $\text{s}^{-1}$ ) on the sample, and measuring the resulting shear stress  $\tau$  (Pa). The viscosity  
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6  $\eta$  (Pa.s) can be calculated by dividing the shear stress by the shear rate.  
7

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

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11 Depending on the temperature, different geometries have to be used. In the first case, the ionic  
12  
13 liquids were characterized in a temperature range between ambient and 60°C, controlled  
14  
15 through a Peltier effect heating plate. The diameter of the plate was such that a 60 mm cone  
16  
17 with 1° truncature could be used, thus allowing accurate measurements to be performed. For  
18  
19 temperatures above 60°C, an oven was used with the rheometer. Due to the oven inner  
20  
21 diameter, these measurements were associated with 25 mm-diameter parallel plate geometry,  
22  
23 with a 1 mm gap between the two plates.  
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31 As the ionic liquids tested have low viscosities, the rheological tests were based on continuous  
32  
33 flow measurements, conducted in a dry nitrogen atmosphere. Due to the high hydrophilic  
34  
35 nature of the PCILs, a dry atmosphere must be used to avoid water pollution, which would  
36  
37 strongly impact on viscosity.  
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#### 42 NMR experiments

43  
44 NMR experiments on the pure PCILs, i.e. free of any added solvent, were carried out on a  
45  
46 Bruker Avance NMR 400 spectrometer equipped with a broadband probe with z-axis gradient  
47  
48 for the measurement of  $^1\text{H}$  and  $^{19}\text{F}$  spectra and the determination of  $^1\text{H}$  and  $^{19}\text{F}$  diffusion  
49  
50 coefficients. Temperatures were controlled within the 300 - 420 K range with a Bruker  
51  
52 BVT3000 system ( $\pm 1$  K regulation). The temperature was calibrated before each set of  
53  
54 measurements by using the standard procedure with a reference ethylene glycol sample.  
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60 PCILs were introduced in 4 mm-diameter NMR tubes and sealed in a glove box under argon

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3 in order to avoid any contact with moisture. Narrow tubes were chosen in order to avoid  
4  
5 convection movements within these low viscosity liquids.  
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8 Self-diffusion coefficients were determined with the pulsed field gradient stimulated echo and  
9  
10 LED sequence using 2 spoil gradients. Self-diffusion coefficients were determined from the  
11  
12 classical relationship  $\ln(I/I_0) = -\gamma^2 D g^2 \delta^2 (\Delta - \delta/3)$  (21) where  $g$  is the magnitude of the  
13  
14 two gradient pulses,  $\Delta$  is the time interval between these pulses,  $\delta$  is their duration,  $\gamma$  is the  
15  
16 gyromagnetic ratio of the nucleus under study and  $I$  and  $I_0$  are the areas of the signals obtained  
17  
18 respectively with and without gradient pulses. The magnitude of the pulsed field gradient was  
19  
20 varied between 0 and  $45 \text{ G} \cdot \text{cm}^{-1}$ ; the diffusion time  $\Delta$  between two pulses was fixed at 200 ms,  
21  
22 and the pulse duration  $\delta$  was set between 3 and 20 ms, depending on the diffusion coefficient  
23  
24 of mobile species.  $\pi/2$  pulse widths were calibrated to  $8.5 \mu\text{s}$  and  $17.5 \mu\text{s}$  for  $^1\text{H}$  and  $^{19}\text{F}$   
25  
26 respectively .  
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### 34 Membrane elaboration

#### 35 *Membranes based on Nafion*

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37 First the Nafion® 117 membrane was immersed in a 2M  $\text{HNO}_3$  aqueous solution and heated at  
38  
39 water reflux temperature for 2 h in order to recover all the Nafion acidic functions ( $\text{Naf-H}^+$ ).  
40  
41 Then, the acidified Nafion membrane, washed several times with deionised water, was  
42  
43 neutralized by the amine constitutive of the PCIL's further used. Neutralization was performed  
44  
45 by immersing the membranes at room temperature for 24 h in a 50/50 v/v mixture of ethanol  
46  
47 and 4M aqueous solution of amine. The membranes were then washed with pure water and  
48  
49 dried for 48 h under vacuum at  $130^\circ\text{C}$ . Then the neutralized membranes were transferred to a  
50  
51 glove box. The dried neutralized membranes were immersed in the corresponding PCIL heated  
52  
53 to  $80^\circ\text{C}$  and PCIL uptake was measured at different times. The PCIL swollen membranes were  
54  
55 removed from the PCIL and kept in the glove box at room temperature for at least a week. The  
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3 weight of the membranes was checked every 24 h over a week in order to evaluate membrane  
4 stability, and more specifically PCIL release from the membrane.  
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### 7 *Membranes based on sulfonated polysulfone*

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10 Sulfonated Polyether sulfone was neutralized by the same amine than that used to synthesize  
11 the PCILs. The synthesis and the characterisation of sulfonated polysulfone were previously  
12 described [23, 24]. Then a mixture of the latter with the selected amount of PCIL was  
13 dissolved in a common solvent i.e. Diethylene glycol monoethyl ether (DGME). After casting  
14 the solution, DGME was evaporated leading to the membrane.  
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### 22 Conductivity measurements

23  
24 Conductivities were determined by electrochemical impedance spectroscopy using an HP  
25 4192A Impedance Analyser in the frequency range 5 Hz - 13 MHz.  
26  
27  
28

29 A conductivity cell consisting of platinum electrodes was filled by the PCIL and closed in a  
30 glove box. The cell constant of c.a.  $1 \text{ cm}^{-1}$  was determined using a standard KCl aqueous  
31 solution. The measurements were carried out from 20°C up to a maximum temperature of  
32 150°C, the temperature being equilibrated for 2h before each measurement.  
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38 The membranes were placed between two stainless steel electrodes under argon (in glove box)  
39 in a Swagelok cell with Teflon joints and spacers, and measurements were performed from  
40 20°C to 150°C. The temperature was equilibrated for 2h before each measurement.  
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45 Membrane thickness was determined with a Digimatic MDG-25SB micrometer by placing the  
46 membrane between two discs.  
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50 The spectra were recorded between 13 MHz and 5 Hz. Due to the high conductivity of PCIL  
51 and their membrane, at high frequency the resistive contribution of the set-up to the overall  
52 resistance (leads and connections) may range from 1 to 10% of the high frequency response of  
53 the membrane. For this reason, the impedances measured are corrected from the set-up  
54 impedance measured in the same frequency range. This impedance can be represented, below  
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3 4 MHz, using an equivalent circuit consisting of an inductance of 5  $\mu\text{H}$  associated with a  
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5 resistance of 1.3  $\Omega$  in series. The resistance of the membrane is taken at the high frequency  
6  
7 intercept with the real axis in the Nyquist plot, which is usually between  $10^6$  and  $10^4\text{Hz}$ .  
8  
9

10 Dynamic mechanical analysis

11  
12 Dynamic mechanical analysis (DMA) measurements were carried out with a TA Instruments  
13  
14 DMA Q800 spectrometer working in the tensile mode. The strain magnitude was fixed at  
15  
16 0.01%. This value ensured that the tests were made in the linear viscoelastic domain.  
17  
18 Measurements were performed in isochronal conditions (1 Hz) and the temperature was varied  
19  
20 between -100 and 150°C at 2°C/min.  
21  
22  
23  
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26

### 27 3. Results and discussion

28  
29 The more convenient chemical route to obtain PCILs involves the neutralisation of a  
30  
31 Brønsted acid by a Lewis base such as aliphatic acyclic or cyclic amine, or an aromatic amine.  
32  
33 Both amine and acid structures modulate PCIL properties. It is hoped that this paper will  
34  
35 contribute to a general discussion of the influence of amine structures on PCIL physico-  
36  
37 chemical properties and, more specifically, on conduction mechanisms in PCILs. For this  
38  
39 purpose, we decided to use one single Brønsted acid, namely trifluoromethanesulfonic, and to  
40  
41 neutralize it with different amines such as primary amines, secondary and tertiary aliphatic  
42  
43 acyclic and cyclic amines. Secondary amines incorporating electron donor atoms such as  
44  
45 oxygen, i.e. ether substituent, or nitrogen, i.e. diamine, were also used. In the latter, only one  
46  
47 amine function was neutralized (Table 1). In addition, with a view to clarifying the impact of  
48  
49 water on PCIL properties and conduction mechanisms, controlled amounts of water were  
50  
51 added. The resulting humidified PCILs were then characterised and discussed. In addition to  
52  
53 the study of PCIL- water blends, the PCIL blends with several host polymers were  
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55 investigated.  
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### 3.1. Anhydrous PCIL physico-chemical properties

#### 3.1.1. Thermal behaviour

The thermal behaviour of PCILs is relevant to their physicochemical properties. Low glass transition and melting temperatures in combination with high thermal stability are the general requirements for good ionic liquids.

As previously observed by Nakamoto *et al* [11], the melting temperature of aliphatic primary amines and aliphatic acyclic symmetrical secondary/tertiary amines (**1-12**) increases with the number of carbons. For PCILs based on cyclic aliphatic ammoniums (**17-23**), the melting temperatures ( $T_m$ ) are higher than those of their acyclic aliphatic ammonium homologues (for example **17** vs **4**). Furthermore, the  $T_m$  of five-membered heterocycles e.g. **17** is higher than that of the six-membered heterocycle e.g. **20**. This behavior can be ascribed to heterocycle geometry and flexibility.

For PCILs resulting from acyclic secondary amines, a much lower  $T_m$  was observed in the case of **13** (BMEA-TF). This might be explained (1) by the flexibility induced by the ether function, and (2) by the interaction between the oxygen lone pair and the ammonium. Indeed, the latter decreases the positive charge on nitrogen and, therefore, decreases ion-ion interactions [17]. Furthermore, the inter- and/or intra-molecular interactions between the ether function and the positive charge might generate a higher local disorder.

Another approach to decrease  $T_m$  [11] consists in preparing PCILs from dissymmetrical amines (**14-16**). In PCILs based on acyclic symmetrical tertiary ammoniums, the increase in ammonium substituent length leads, except for TEA-TF (**6**), to a  $T_m$  increase. Surprisingly, **6** exhibits the lowest  $T_m$  of overall PCILs based on aliphatic acyclic ammonium. For the tertiary cyclic ammonium, the increase in asymmetry, resulting from the exocyclic substituent and its length, induces a sharp decrease of  $T_m$  that drops to 6°C for BuPyrA-TF. As observed

1  
2  
3 for BMEA-TF, the presence of an ether function in a five-membered cycle i.e. morpholinium  
4  
5 (23) decreases  $T_m$  (23 vs 22). In this heterocyclic ammonium, the  $T_m$  decrease cannot be  
6  
7 ascribed to a possible flexibility induced by the ether function, and the decisive factor should  
8  
9 be the interaction between the lone pair and the ammonium.  
10  
11

12  
13 While the ether oxygen lone pair cannot result in stable oxoniums, by reacting with  
14  
15  $H^+$ , the situation is completely modified when the lone pair is carried by a much stronger  
16  
17 Brønsted base e.g. amine as in diamines.  
18

19  
20 Thus promising PCILs were obtained by neutralization of triflic acid (TF) with different  
21  
22 diamines,  $H_2N-R-NH_2$  (R= alkyl). The neutralization of both amino groups leads to very high  
23  
24  $T_m$ s, which are unsuitable in PEMFC, while the diamine half-neutralization seems very  
25  
26 attractive.  $T_m$  is not only much lower than that for diammonium but also than those of most  
27  
28 of the monoammonium-based PCILs.  $^1H$  NMR spectra did not allow the presence of free  
29  
30 amine to be observed, reflecting the fact that the proton interacts with both amino groups of  
31  
32 the diamine. This interaction, which delocalises the positive charge between two nitrogen  
33  
34 atoms, might be intra and/or inter-molecular (figure 1). By generating disorder, these  
35  
36 interactions decrease  $T_m$ . At this stage, it is frustrating to realise that we are unable to  
37  
38 discriminate between intra and intermolecular chelation of the proton. This probably depends  
39  
40 on the length of R and we therefore intend to perform comparative *ab initio* calculations to  
41  
42 determine the more plausible interactions, depending on R length.  
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50  
51 Figure 1.

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53 With regard to the  $T_g$  values of these PCILs, the high melting points obtained for  
54  
55 symmetrical salts (1-12) indicate their capacity to crystallize. As previously observed by  
56  
57 Watanabe [11] and Angell [14] (for series of primary, secondary and ternary ammonium  
58  
59 salts), the excessive crystalline character of symmetrical salts prevents an accurate  
60



1  
2  
3 determination of Tgs, even after melting and soaking PCILs in liquid nitrogen. Thus Tgs were  
4  
5 only determined for a few of our PCILs.  
6

7  
8 As for thermal stability characterized by TGA experiments, it has been shown that not all  
9  
10 monoammonium-based PCILs undergo weight loss up to at least 300°C. On the contrary,  
11  
12 diamine-based PCILs undergo weight loss from lower temperatures. Indeed such weight loss  
13  
14 occurs in two stages i.e. 240 and 500°C for **25**. At 240°C, the weight loss is around 13%. It  
15  
16 might correspond to a thermally activated disproportionation of PCIL into diammonium and  
17  
18 starting diamine. The latter can obviously evaporate but it must be emphasized that the weight  
19  
20 loss occurs at a temperature exceeding, from about 100°C, the boiling point of the diamine.  
21  
22 Taking into account this thermal event, there may be a risk that the preliminary purification of  
23  
24 diamine-based PCIL, involving its thermal drying (at 100°C under vacuum), will lead to its  
25  
26 partial disproportionation resulting in diamine evaporation. Nevertheless, neither <sup>1</sup>H NMR nor  
27  
28 elemental analyses revealed any removal of diamine relating to the purification process.  
29  
30  
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36 Table 1

### 37 38 3.1.2. Viscosity and conductivity

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40 PCIL conductivity depends on both ion concentration and viscosity. Indeed, high volumic  
41  
42 concentration in PCIL favors conductivity but, at the same time, leads to high density. The  
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44 densities of triflate-based PCILs range between 1.2 and 1.7 and are close to the reported data  
45  
46 [24]. Density variation is related to both steric hindrance around the ammonium and ion  
47  
48 concentration. The more hindered the ammonium, the lower its density. This is reflected in  
49  
50 the lengthening of the alkyl substituent of the ammonium salt. In order to calculate the density  
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52 at 130°C, a linear expression proposed in the literature [19, 21] was used.  
53  
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55  
56

57  
58 As conductivity depends on ionic mobility, which in turn is dependent on viscosity, a  
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60 rheological analysis is indispensable in order to assess the influence of viscosity on

1  
2  
3 conductivity. Viscosity is dependent on ion-ion interactions, Van der Waals interactions and  
4  
5 hydrogen bonding (increased interaction leading to higher viscosities), but also on molecular  
6  
7 weight. Some of the PCILs, although well-adapted to membranes operating at 130°C, have  
8  
9 unfortunately high melting points making viscosity measurements impossible. The viscosity  
10  
11 data of the others are compatible with findings in the literature [27]. For PCILs originating  
12  
13 both from dissymmetrical amines and diamines, viscosities increase with alkyl chain lengths.  
14  
15 The viscosities of PCIL decrease with the starting amine according to dissymmetrical  
16  
17 monoamines < symmetrical monoamines < diamines. The high viscosities of PCILs,  
18  
19 originating from half-neutralized diamines, are mainly related to intermolecular interactions  
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21 but also, to a lesser extent, to their assumed higher dissociation degree. The latter, due to the  
22  
23 high donor number of the un-neutralized amino group and to its polarity, should indeed be  
24  
25 higher for this PCIL series. For **13** (BMA-TF), taking into account the presence of oxygen,  
26  
27 viscosity increases with regard to the other PCILs based on monoammoniums can be  
28  
29 expected. This gain in viscosity, due to intermolecular interactions for **13** (BMA-TF), should  
30  
31 partly counterbalance the decrease in viscosity related to the high flexibility induced by the  
32  
33 ether function.  
34  
35

36  
37 The maximum conductivity gap, at 130°C, between PCILs obtained from symmetrical or  
38  
39 dissymmetrical amines, is limited and reaches only a factor of 1.5 (Table 1, Figure 2 a). As  
40  
41 expected the conductivity dependence on temperature of monoammonium based PCILs  
42  
43 exhibits VTF type behaviour with pseudo-energy activation ranging between 2 and 5 KJ.mol<sup>-1</sup>  
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53 Due to the high viscosities, fairly low conductivities were expected for PCILs obtained from  
54  
55 half-neutralized diamines. Surprisingly, **24-25** exhibit conductivities close to those of the less  
56  
57 viscous monoammonium-based PCILs. Contrary to monoammoniums, conductivity  
58  
59 dependence on temperature of half-neutralized diamine-based PCILs (Figure 2b) is not a very  
60

1  
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3 good match with classical VTF behaviour. From these results, it might be inferred that, in  
4  
5 half-neutralized diamine-based PCILs, conduction is not exclusively vehicular as in  
6  
7 monoammonium-based PCILs.  
8  
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10  
11  
12 Figure 2.  
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### 14 3.1.3. Self-Diffusion Coefficient

15 PFG-NMR was used to investigate the structure of these liquids by measuring a dynamic  
16  
17 property (on a macroscopic space scale of 1-100  $\mu\text{m}$ ). Thus, the self-diffusion coefficients of  
18  
19  $\text{H}^+$  ( $D_{\text{H}^+}$ ), amine ( $D_{\text{am}}$ ), ammonium ( $D_{\text{am}}$ ) and the anion ( $D_{\text{anion}}$ ) were measured in these  
20  
21 different systems by PFG-NMR. Their temperature-dependence, between PCIL  $T_m$  and 420  
22  
23 K, is compared in figure 3. Table 2 gathers, at 400K, the diffusion coefficients of several  
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25 PCILs.  
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31

32 Table 2.

33  
34 Figure 3.

35  
36 From Table 2 and Figure 3, two observations may be made about the  $\text{H}^+$  diffusion mechanism.  
37  
38 Firstly, with regard to PCILs based on monoammoniums, in which the diffusion coefficients  
39  
40 of  $\text{H}^+$  and the amine cannot be discriminated, it can be seen that cationic conduction is  
41  
42 exclusively ensured by the ammonium. When ammonium bulkiness increases, the difference  
43  
44 between  $D_{\text{amine}}$  and  $D_{\text{anion}}$  becomes very slight, in agreement with the size effect on the  
45  
46 diffusion described by Watanabe [10].  
47  
48  
49

50 Secondly, unlike the previous PCILs, those resulting from a half-neutralization of diamines,  
51  
52 **24-26** exhibit two distinct diffusion coefficients i.e.  $\text{H}^+$  and diamine. This means that, in  
53  
54 addition to the previous vehicular mechanism, another conduction mechanism, i.e. a  
55  
56 Grotthuss-like mechanism, takes place as in imidazole/ HTFSI PCIL [28]. The existence of  
57  
58 both conduction mechanisms helps explain why high conductivities can be obtained for this  
59  
60



From the diffusion coefficients, the cationic transference numbers were calculated from eq.6.

$$t^+ = \frac{D_{H^+}}{D_{H^+} + D_{anion}}$$

The cationic transference numbers of monoammonium based PCILs are close to 0.5, with the highest, 0.56, being obtained for PCIL 6 in accordance with the relatively small size of the ammonium. When ammonium size increases,  $T^+$  tends to be equal to 0.5. For these PCILs  $T^+$  is almost constant vs temperature. For the PCILs based on half-neutralized diamines,  $T^+$  is appreciably higher than 0.5 and decreases when the temperature increases. These higher  $T^+$  and the fact they decrease with higher temperatures (Figure 4) are probably respectively related to the Grotthuss mechanism and the increase in vehicular contribution with temperature.

Figure 4.

#### 3.1.4. Electrochemical stability

The electrochemical stability of PCILs was mainly characterized by cyclic voltammetry (CV), performed in acetonitrile + 0.1M TBAP as electrolyte (see experimental section). Their electrochemical behaviour was compared to that of the starting amine.

#### PCILs from monoamine

Concerning the starting amine, it is well known that amine can be oxidized through an irreversible electron oxidation process leading to an intermediate radical cation according to next equation [29].



For all the amines used, the CVs exhibit one anodic peak at  $E_{pa}$  whose value essentially depends on the amine structure i.e. the number and structure of nitrogen substituents. Thus figure 5 shows that the  $E_{pa}$  value is lowest for a tertiary amine (TPrA) at 1.09, higher for a

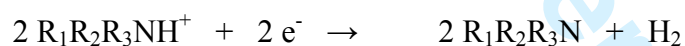
1  
2  
3 secondary amine (DPrA) at 1.35, and highest for a primary amine (PrA) at 1.92. It must be  
4 emphasized that the order of Epa values is in fairly good agreement with the order of the  
5 inductive electron-donating effect exerted by the alkyl substituents of the nitrogen atom.  
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11  
12 Figure 5:

13  
14 In the case of PCILs, protonation of the monoamines leads to the disappearance of the  
15 oxidation peak of the free amines attesting to their purity, whereas no other oxidation process  
16 is detectable up to 2.5 V/SHE (Figure 6).  
17  
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24 Figure 6

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26 In the cathodic region, the quasi reversible reduction of the ammonium salt is observed. This  
27 process corresponds overall to the reduction of the proton, generating H<sub>2</sub>.  
28  
29



33  
34 E<sub>1/2</sub> values connected with the basicity of the starting amines were expected. However, due to  
35 adsorption phenomena on the platinum electrode [29, 30] coupled to the electron transfer,  
36 distortions of the CVs were observed, making it fairly difficult to accurately determine E<sub>1/2</sub>.  
37  
38 This is illustrated by the CV comparison of PCILs **7**, **12** and **9** whose E<sub>1/2</sub> values are close  
39 (0.67, 0.69, 0.65 respectively). Nevertheless, from **7** (PrA-TF) up to **9** (TrPA-TF) the  
40 electron-donating effect increases with the number of alkyl substituents and should make the  
41 reduction process more difficult. This adsorption process is particularly evidenced by the high  
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ΔE<sub>p</sub> value for **7**, **14-16**, which is higher than 300 mV.

### PCILs from diamines

Two successive nitrogen oxidation processes were expected in diamines. In fact, the CVs  
show a single broad irreversible anodic peak at Epa around 1.5V/SHE. It may be suggested

1  
2  
3 that the wide breadth of this signal indicates that the two one-electron nitrogen-centred  
4  
5 transfers are superimposed.  
6

7  
8 The PCILs based on half-neutralized diamines have both a free amino group and a protonated  
9  
10 one. Thus, their CVs show one irreversible anodic and one quasi reversible cathodic process.  
11  
12 The oxidation peak remains very broad, whereas the half-protonation shifts the Epa towards  
13  
14 to a more positive value at around 1.9V/SHE (Figure 7).  
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20 Figure 7

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22 This result seems to prove that when one amino group is neutralized, the proton is not  
23  
24 exclusively located on one amino group of the PCILs and that it interacts with both, through a  
25  
26 fast protonic equilibrium. Depending on the structure of the PCILs, this interaction may be  
27  
28 either intramolecular for short N to N distance (DAEt-TF, **24**) or intermolecular when the  
29  
30 alkyl chain separating the amino groups increases (DADc-TF, **26**). It should be noted that this  
31  
32 protonic exchange has been clearly observed by  $^1\text{H}$  and  $^{15}\text{N}$  NMR analyses, as previously  
33  
34 described, since labile protons (i.e. of  $\text{NH}_2$  and  $\text{NH}_3^+$  moieties) appear as a single well-defined  
35  
36 signal.  
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39  
40 In the cathodic region, these PCILs behave similarly to monoammonium-based PCILs. Here  
41  
42 again, the  $E_{1/2}$  value and the shape of the CVs strongly depend on the nature of the PCIL  
43  
44 (Figure 6). Here, it can be assumed that the adsorption process coupled to the electron transfer  
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46 is more intense than that observed for monoammoniums since  $\Delta E_p$  values higher than 500  
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48 mV are observed.  
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## 52 53 54 55 **3.2. PCIL blends**

### 56 57 3.2.1. Humidified PCILs

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3 Prior to any characterization, PCILs were thoroughly dried, given that the presence of water,  
4 even at very low concentrations, is expected to have an impact on PCIL properties e.g.  
5 conductivity. In order to quantify this impact we investigated the blends of (TEA-TF, **6**) and  
6 water. To express the water content, we will use the ratio (in moles)  $x/y$ , where  $x$  is the  
7 number of moles of water and  $y$  the number of moles of PCIL. In table 3 are gathered the  
8 viscosities, conductivities and diffusion coefficients at 40 and 80°C of these blends. It can be  
9 emphasized that water has a distinct impact on the PCIL characteristics. Following water  
10 uptake, conductivity increases due to water's outstanding properties, namely 1) its very low  
11 viscosity that decreases the viscosity of the blend PCIL/water, 2) its high dielectric constant  
12 that favours ion-pair dissociation, 3) its highly solvating ability reflected by its Donor Number  
13 DN, close to that of tetrahydrofuran, and its high Acceptor Number AN, 4) its molecules that  
14 can significantly contribute to proton mobility.  
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32 Table 3.

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34 In fully dried TEA-TF PCIL, the proton and amine have close diffusion coefficient values. At  
35 low water concentration, 1/10, and at temperatures below 80°C, the diffusion coefficients  
36 (amine, anion and proton) slightly increase in relation to those of the dry sample, and seem to  
37 be proportional to the decrease in viscosity. Moreover, the water diffusion coefficient ( $D_{H_2O}$ )  
38 is much higher than those of the PCIL components. This is related to the very low molecular  
39 weight of water with regard to the ammonium and triflate anion. For this blend, and up to  
40 80°C, a vehicular mechanism involving ammonium, as in dried PCIL, can be assumed. On  
41 the other hand, above 80°C, a new proton diffusion coefficient appears whose value is  
42 intermediate between that of the water and that of the amine. It may therefore be assumed that  
43 from 80°C a rapid proton exchange takes place between the amine and water and that the  
44 proton migrates via both a Grotthuss mechanism (the proton jumping between water-amine,  
45 water-water or amine-amine) and a vehicular mechanism involving ammonium and oxonium.  
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3 For higher water concentrations, the mixed proton-conducting mechanism (Grotthuss-  
4 vehicular) starts from lower temperatures. Thus for the blend 1/1 the diffusion coefficient of  
5  
6  $H^+$  is very close to that of water, and much higher than that of amine.  
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### 10 3.2.2. PCILs –Polymer blends

11  
12 Due to their ionic liquid nature, PCILs must be hosted in a polymer to provide the  
13 indispensable mechanical properties that any PEMFC membrane must offer.  
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15  
16 Taking into account the thermomechanical requirements of a membrane operating at  $T \geq$   
17  
18  $130^\circ\text{C}$ , the host polymer must exhibit high chemical, electrochemical, thermal and mechanical  
19 stabilities. Furthermore, the PCIL uptake must be high enough to result in highly anhydrous-  
20 proton conducting membranes. Two kinds of polymeric backbones can operate over long  
21 periods at such temperatures, those using fluorinated or high performance polymers. Both  
22 polymers can be used in their non-ionic and ionic forms.  
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#### 34 *PCILs hosted by neutral polymers*

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36 PVDF-based copolymers, namely polyvinylidene fluoride-co-polyhexafluoropropene  
37 PVDF-HFP, have been observed to be good host polymers for PCILs [31]. However, the  
38 authors observed a confinement of PCILs, high conductivities only being obtained at high  
39 PCIL uptake. However, this makes the thermomechanical performances of these membranes  
40 at high temperatures questionable. We attempted unsuccessfully to blend PCILs with high-  
41 performance non-ionic polymers such as polyethersulfone (UDEL or RADEL® grades) or  
42 polyether-ether ketone PEEK. The poor affinity of these polymers for the ionic liquids  
43 resulted in insignificant PCIL uptakes.  
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#### 58 *PCILs hosted by ionomers*

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3 We observed fairly good combinations of mechanical and conductive performances  
4 for blends of Nafion 117 ® [19, 20, 21] with PCILs. In order to avoid the release of molecular  
5 acids resulting from H<sup>+</sup>/ammonium exchange, Nafion 117 was first neutralized with the same  
6 amine as used to prepare the PCIL. The storage modulus, E' above 120°C, was, however, in  
7 the range of 1 to 3 MPa. Mixing neutralized Nafion 117 with the PCILs based on mono-  
8 ammonium cation, reported in this paper, results unfortunately in the same behaviour,  
9 regarding conductivity and E', as observed in our previous reports [19, 20, 21]. Although  
10 these E' values seem too low to allow using Nafion as a host polymer for high-temperature  
11 PEMFC membranes, they are high enough to allow using PCIL hosted by Nafion in the  
12 electrode active layers.

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27 When Nafion 117 is neutralized by diamines, a neat increase of E' is observed, as  
28 shown in Figure 8. This compares the thermal evolution of E' for Nafion neutralized by either  
29 a monoamine or several diamines H<sub>2</sub>N-(CH<sub>2</sub>)<sub>n</sub>-NH<sub>2</sub>. These high E' values, which originate  
30 from the physical cross-linking of Nafion, are much higher than those of monoammonium-  
31 based Nafion. Thus, at 130°C, E' reaches 434 MPa for n = 2 and progressively decreases  
32 down to 151 MPa for n = 6. Following PCIL uptake, a sharp E' decrease is observed. E' close  
33 to 110 MPa was measured for n= 2 while, for n > 2, E' drops to 10-17 MPa. Conductivity is  
34 strongly decreased by the Nafion cross-linking and ranges between 2 and 5mS/cm at 130°C  
35 for PCIL uptake of 40%. However, membrane reinforcement, allowing the membrane to be  
36 shaped in thinner films, will counterbalance the effect of the conductivity drop on internal  
37 resistance.

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53 Figure 8.

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55 Other ionomers based on High Performance polymeric backbones were also evaluated.  
56 Thus, a sulfonated polysulfone ionomer, having an Ionic Exchange Capacity of 1.3 meq/g,  
57 was blended by PCILs. High PCIL uptakes were observed with various PCILs, which was  
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3 not the case for the non-ionic polymer. A plasticizing effect was observed that decreases  
4 ionomer stiffness. Unfortunately, membrane conductivity hardly reaches the millisiemens per  
5 cm. Compared with the conductivities of membranes based on neutralized Nafion, those of  
6 membranes based on neutralized sulfonated polysulfone are much lower. From these data, it  
7 might be inferred that in Nafion most of the PCILs are located in ionic channels while, in  
8 sulfonated polysulfones, PCILs are confined to the vicinity of the polymeric backbone.  
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#### 20 **4. General discussion: Future prospects for PCIL-based membranes**

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24 In today's PEMFCs that operate below 80°C, the membrane consists of an ionomer.  
25 The ionic moieties cannot therefore be eluted by the water flux that comes from both the  
26 electrochemical reaction and the gas humidifiers. However, in a PEMFC with H<sub>3</sub>PO<sub>4</sub> and  
27 PCIL-based membranes, the proton-conducting moiety would be removed when the PEMFC  
28 operates below 100°C. On the other hand, above 120°C, the PEMFC produces water at the  
29 vapour state, so that the release of molecular proton-conductors as H<sub>3</sub>PO<sub>4</sub> and PCIL need not  
30 be a concern. The ideal solution, even though it seems illusory, should consist in keeping high  
31 conductivities while using fully hydrophobic PCILs to operate PEMFCs from -20° up to  
32 temperatures higher than 120°C. A pragmatic solution for EV implementation should  
33 therefore consist in hybridizing PEMFCs with batteries in order to maintain PEMFCs at  
34 120°C. This implies that PEMFCs have to be started and stopped at 120°C.  
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51 Although membranes with a good combination of mechanical properties and  
52 conductivities have recently been obtained (patent pending), several issues still remain. The  
53 first concerns the degree of purity of PCILs produced on an industrial scale. Indeed PCILs,  
54 liquids at sub-ambient temperature, can be neither distilled nor crystallized. In the case of an  
55 operation above 120°C, however, this problem can be solved by selecting PCILs from among  
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3 those whose melting point is around 30-40°C. As a matter of fact, they could easily be  
4 purified by recrystallization.  
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8 Another issue relates to the production on the cathode of amine that may be removed  
9 by evaporation. To prevent this elimination, an excess of non-volatile acid might be used,  
10 provided this molecular acid damages neither the membrane nor the electrodes and is  
11 perfectly miscible with the PCIL. The use of half-neutralized diamines appears an attractive  
12 solution, as it will limit, but not eliminate, the risk of removal related to a disproportionation  
13 of the monoammonium into a mixture of diamine and diammonium. Special attention must  
14 therefore be paid to the boiling point of the diamine, which should be as high as possible.  
15 Lastly an adsorption on the electrocatalyst of the amines, which might be assimilated to  
16 poisoning, may be a problem. Decreasing the amine basicity and increasing the steric  
17 hindrance around the nitrogen should be envisaged in view to avoid, or at least drastically  
18 limit, this adsorption.  
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34 Despite these issues, PCIL-based membranes have indisputable assets and remain  
35 among the most plausible candidates for High Temperature PEMFCs. In addition to their high  
36 conductivity at the anhydrous state, which will be appreciably enhanced by the unavoidable  
37 trapping of part of the water produced by the PEMFC, these hydrophilic PCILs should  
38 prevent, or at least limit, the degradation of the mechanical performance of the fairly  
39 hydrophobic polymeric backbone. Indeed, most of the oxidative by-products of the PEMFC  
40 are hydrophilic and should, if possible, remain in the PCILs. It might be assumed that, owing  
41 to the high content of PCILs, the impact of their possible (but limited) degradation on the  
42 membrane lifespan should be markedly lower than in classical membranes.  
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54 To conclude, research in this new scientific field should focus on highly stable  
55 (chemical, electrochemical, thermal) PCILs, which are easy to purify into an electrochemical  
56 grade and should provide, once blended to functional polymers, an optimal combination of  
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3 mechanical and conductive properties. From an academic point of view, this new research  
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5 field is very demanding in terms of the understanding of conduction mechanisms.  
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## 10 11 12 **5. Conclusion** 13 14 15 16

17 This contribution that gathers the physico-chemical characterizations of a wide variety  
18 of ammoniums based Proton-Conducting Ionic Liquids allows emphasizing the high  
19 complexity of these molecular salts. While the general trend is the preparation of PCILs  
20 exhibiting high conductivities in a wide temperature range, we voluntarily selected crystalline  
21 salts. As a matter of fact (i) the targeted application deals with PCIL based membranes  
22 operating only at temperatures higher than 100°C, in order to avoid any PCIL removal by  
23 liquid water produced by the PEMFC and (ii) their crystalline nature allows expecting an easy  
24 scale-up of the PCIL purification by recrystallization. Although the amount of water trapped  
25 by a PEMFC membrane operating at  $T > 120^{\circ}\text{C}$  cannot be assessed, part of the water  
26 produced by the PEMFC will presumably impregnate the membrane. The investigation of the  
27 water influence on the PCILs properties shows that viscosity sharply decreases in presence of  
28 water, while conductivity and diffusion coefficients significantly increase. In addition, water  
29 intrinsically contributes to the conductivity enhancement, through a Grotthuss-like  
30 mechanism that has been unambiguously evidenced. Therefore, the unavoidable  
31 humidification of the membrane, during the PEMFC operation, will level out the PCILs  
32 performances.  
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54 The more promising results deal with half-neutralized diamine based PCILs, whose  
55 conduction proceeds by both vehicular and Grotthuss-like mechanisms. In addition, despite  
56 their high viscosity, these PCILs exhibit high conductivity and cationic transference number  
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3 at 130°C. Lastly, they were found to reinforce markedly, through physical cross-linking, the  
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5 Nafion based membranes.  
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10 **Acknowledgements:** the authors express their gratitude to ANR PAN-H and ERAS-Labo that  
11  
12 respectively granted the national project CLIPPAC and the PhD thesis of Mathieu Martinez.  
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**Figure and table captions.**

Table 1. PCILs physical characteristics.

Table 2. Self diffusion coefficients, transference numbers ( $T^+$ ), NMR calculated conductivities ( $\sigma_{\text{calc}}$ ), and dissociation for some CLIPs at 130°C.

Table 3. Viscosities, conductivities and self diffusion coefficients of blends of **6** (TF-TEA) and water.

Figure 1: Inter and intra-molecular hydrogen bonding involved in half neutralized diamines.

Figure 2: Conductivity vs reciprocal temperature a) monoammonium based PCIL (**15**), b) half neutralized diamine based PCIL (**24**)

Figure 3: Self diffusion coefficients of **16** and **24**.

Figure 4: Transference numbers vs temperature for monoammonium based CLIP (**15**), and half neutralized diamine based PCIL (**24**)

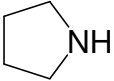
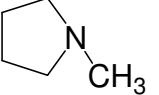
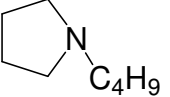
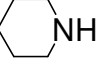
Figure 5: Cyclic voltammetry on platinum electrode (diam. 5mm) of monoamines involved in PCIL's (2 mM) in  $\text{CH}_3\text{CN} + 0.1\text{M TBAP}$ ,  $v = 100 \text{ mV}\cdot\text{s}^{-1}$ .

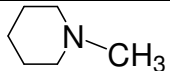
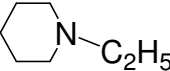
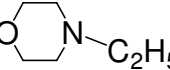
Figure 6: Cyclic voltammetry on platinum electrode (diam. 5mm) of monoammonium based PCIL's (2 mM) involving monoamines in  $\text{CH}_3\text{CN} + 0.1\text{M TBAP}$ ,  $v = 100 \text{ mV}\cdot\text{s}^{-1}$ .

Figure 7: CV of 2 millimolar DAPr-TF (**24**) in  $\text{CH}_3\text{CN} + 0.1\text{M TBAP}$  on platinum electrode (diam. 5mm),  $v = 100 \text{ mV}\cdot\text{s}^{-1}$ .

Figure 8: Storage modulus vs temperature of Nafion neutralized by mono and diamines.

Table 1.

Amine	issue	PCIL code	T <sub>m</sub> (°C)	T <sub>deg</sub> (°C)	density (130°C)	η at 130°C (mPa.s)	σ (mS/cm) at 130°
(CH <sub>3</sub> ) <sub>2</sub> NH	1	DMA-TF	114	390	b	b	c
(CH <sub>3</sub> ) <sub>3</sub> N	2	TMA-TF	150	380	b	b	c
C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub>	3	EA-TF	173	400	b	a	c
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH	4	DEA-TF	127	390	b	6	d
(CH <sub>3</sub> ) <sub>2</sub> CHNH <sub>2</sub>	5	isPr-TF	180	395	b	b	c
(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	6	TEA-TF	36	380	1.33	14	31
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	7	PrA-TF	176	385	b	b	c
(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> NH	8	DPrA-TF	136	390	b	7	c
(C <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> N	9	TPrA-TF	160	380	b	b	c
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> NH <sub>2</sub>	10	BuA-TF	178	380	b	b	c
(C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> N	11	TBuA-TF	128	383	b	d	c
(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> NH	12	DBuA-TF	140	390	b	b	c
(C <sub>2</sub> H <sub>4</sub> - O - CH <sub>3</sub> ) <sub>2</sub> NH	13	BMEA-TF	55	300	1.41	6	27
CH <sub>3</sub> -CH <sub>2</sub> -NH-CH <sub>3</sub>	14	EtMA-TF	90	385	1.62	3.79	50
CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>3</sub> -NH-CH <sub>3</sub>	15	MBuA-TF	70	380	1.45	4.16	30
CH <sub>3</sub> -(CH <sub>2</sub> ) <sub>3</sub> -NH-CH <sub>2</sub> -CH <sub>3</sub>	16	EtBuA-TF	78	390	1.30	5.13	23
	17	Py-TF	157	395	b	b	c
	18	MetPy-TF	103	382	b	d	30
	19	BuPy-TF	6	390	1.30	4.9	32
	20	Pir-TF	145	390	b	b	c

	<b>21</b>	MetPir-TF	101	380	b	d	28
	<b>22</b>	EtPir-TF	59	382	d	d	30
	<b>23</b>	EtMph-Tf	44	375	d	d	27
NH <sub>2</sub> -(CH <sub>2</sub> ) <sub>2</sub> -NH <sub>2</sub>	<b>24</b>	DAEt-TF	78	240	1.60	27	35
NH <sub>2</sub> -(CH <sub>2</sub> ) <sub>3</sub> -NH <sub>2</sub>	<b>25</b>	DAPr-TF	36	260	1.60	40	45
NH <sub>2</sub> -(CH <sub>2</sub> ) <sub>10</sub> -NH <sub>2</sub>	<b>26</b>	DAD-TF	49	250	1.22	81	7

a: cannot be determined due to the high crystalline character ; b: too high melting point to be investigated ;  
 c:  $\sigma$  less than  $10^{-3}$  mS.cm<sup>-1</sup>; d: not carried out.

Table 2.

Sample code	$D_{H^+}$ ( $\text{cm}^2\text{s}^{-1}$ )	$D_{am}$ ( $\text{cm}^2\text{s}^{-1}$ )	$D_{anion}$ ( $\text{cm}^2\text{s}^{-1}$ )	$T^+$	$\sigma_{calc}$ ( $\text{Scm}^{-1}$ )	$\sigma_{exp}$ ( $\text{Scm}^{-1}$ )	Dissociation rate
6 (TEA-TF)	$3.9 \times 10^{-6}$	$3.6 \times 10^{-6}$	$3.0 \times 10^{-6}$	0.56	0.1	0.030	0.30
13 (BMEA-TF)	$2.0 \times 10^{-6}$	$2.2 \times 10^{-6}$	$2.2 \times 10^{-6}$	0.49	0.067	0.027	0.40
24 (DAE-TF)	$1.90 \times 10^{-6}$	$1.36 \times 10^{-6}$	$1.18 \times 10^{-6}$	0.51	-	0.035	-
25 (DAPr-TF)	$4.50 \times 10^{-6}$	$3.85 \times 10^{-6}$	$3.13 \times 10^{-6}$	0.58	-	0.046	-
13 (EtMA-TF)	$5.11 \times 10^{-6}$	$5.01 \times 10^{-6}$	$4.22 \times 10^{-6}$	0.55	0.092	0.025	0.27
14 (BuMA-TF)	$3.77 \times 10^{-6}$	$3.767 \times 10^{-6}$	$3.71 \times 10^{-6}$	0.5	0.067	0.016	0.24
15 (BuEtA-TF)	$2.97 \times 10^{-6}$	$2.94 \times 10^{-6}$	$2.93 \times 10^{-6}$	0.5	0.058	0.015	0.26

Table 3.

x/y mol/mol	$\eta$ (mPa.s)		$\sigma$ (mS/cm)		$D_{am.}$		$D_{H^+}$		$D_{anion}$		$D_{H_2O}$	
	40°C	80°C	40°C	80°C	(cm <sup>2</sup> s <sup>-1</sup> ) x10 <sup>-6</sup>		(cm <sup>2</sup> s <sup>-1</sup> ) x10 <sup>-6</sup>		(cm <sup>2</sup> s <sup>-1</sup> ) x10 <sup>-6</sup>		(cm <sup>2</sup> s <sup>-1</sup> ) x10 <sup>-6</sup>	
0	36	16	10	20	0.28	1.20	0.28	1.20	0.22	1	a	a
1/10	34	13	11	23	0.50	2.40	0.50	8.40	0.45	2.20	3.45	19
1/5	33	12	12	24	c	c	c	c	c	c	c	c
1/2	31	12	14	26	0.80	4.20	b	b	0.70	3.60	b	b
1/1	21	10	17	30	.88	5.40	6.50	b	0.88	5.44	5.50	b

a: anhydrous PCIL, b: not possible to measure (peak to large) c: not carried out

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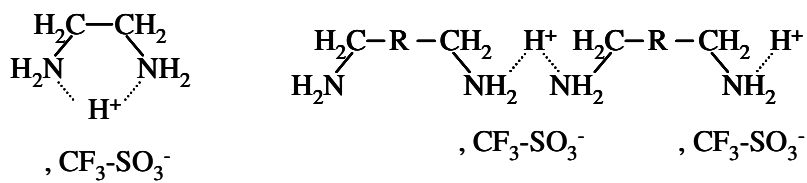
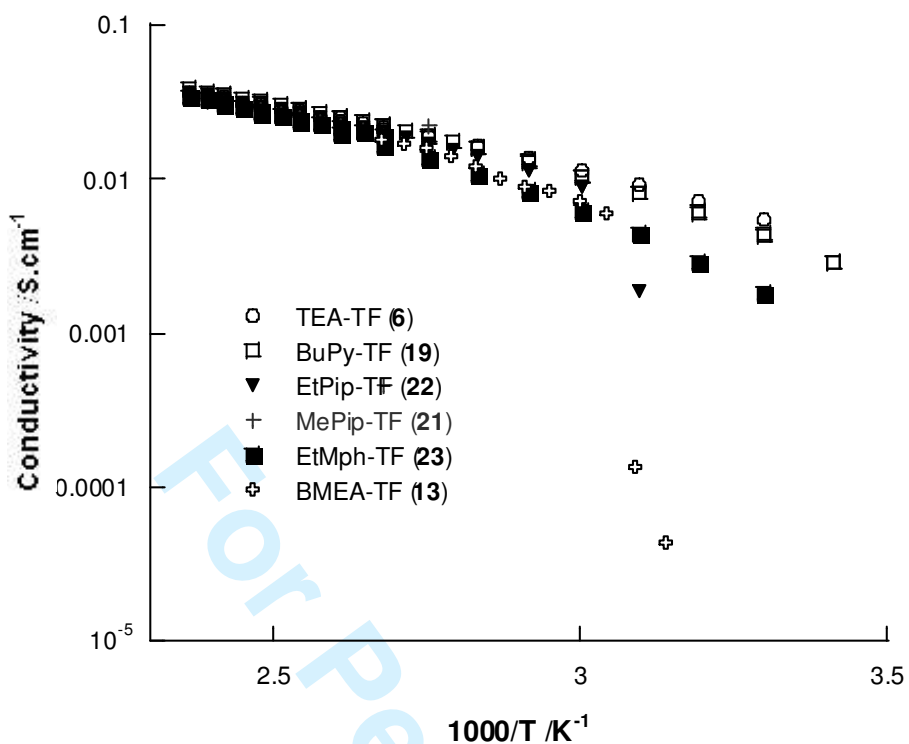
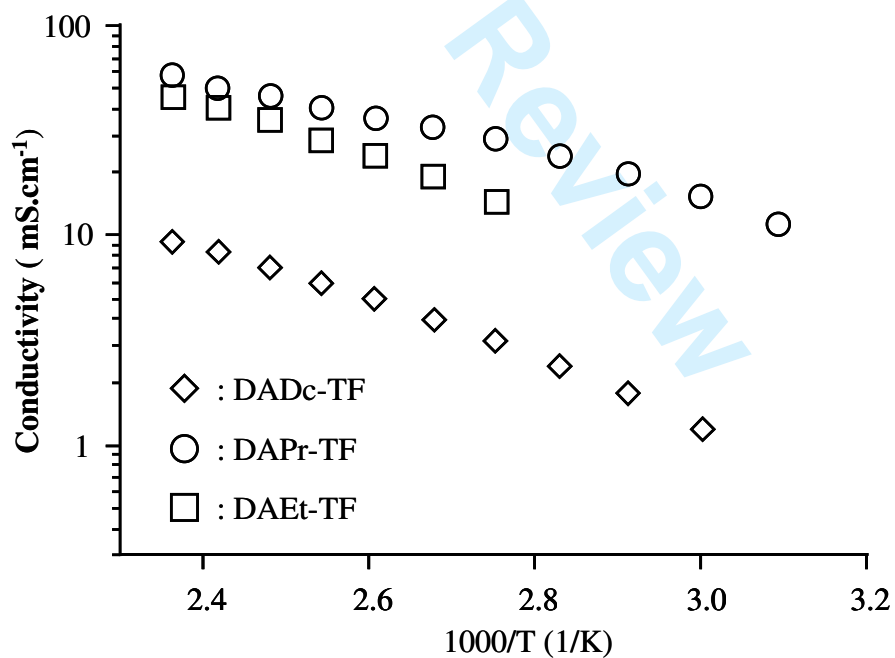


Figure 1

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b)  
Figure 2



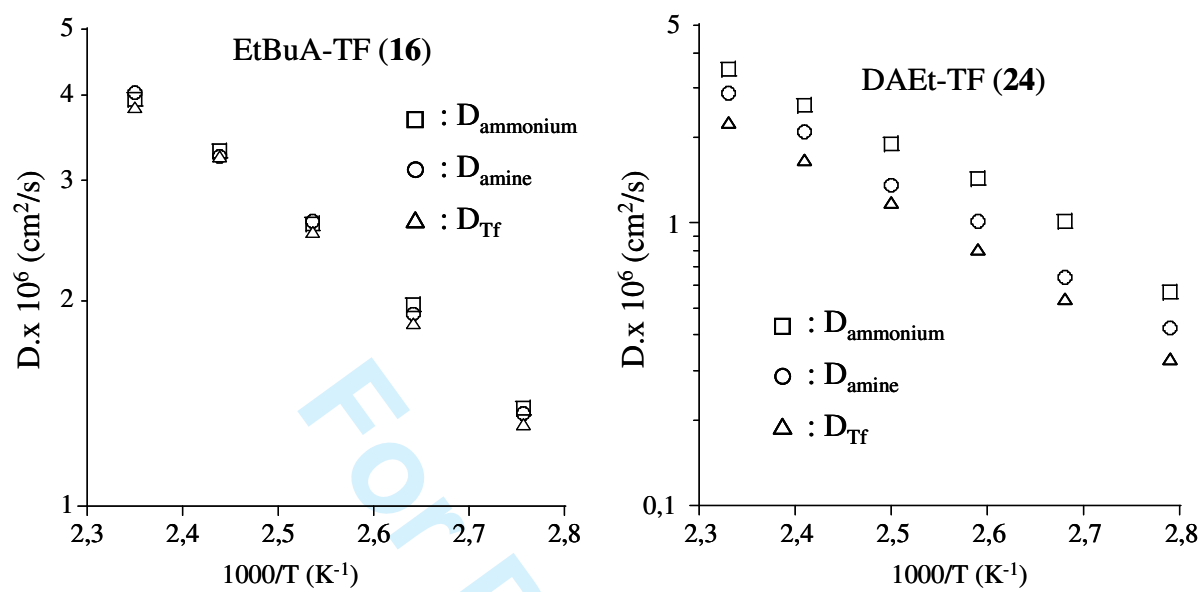


Figure 3

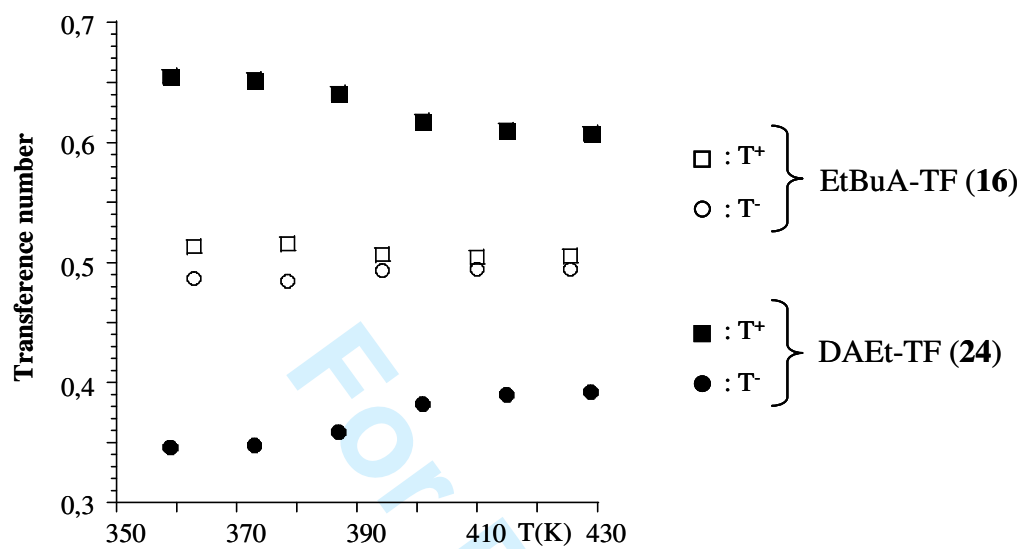


Figure 4

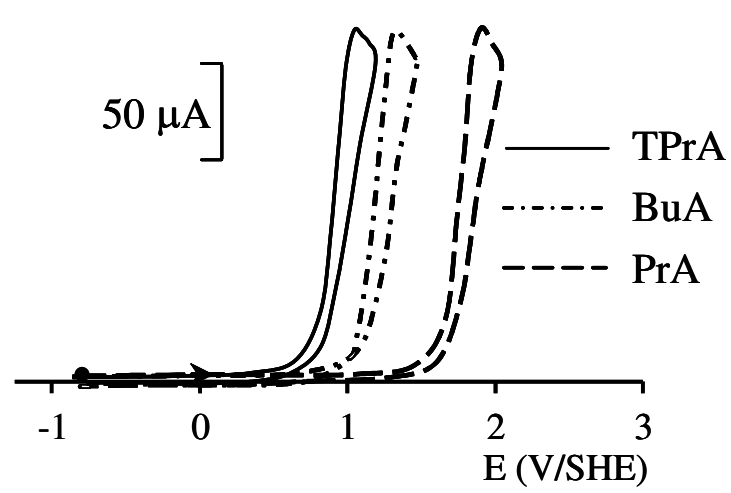


Figure 5

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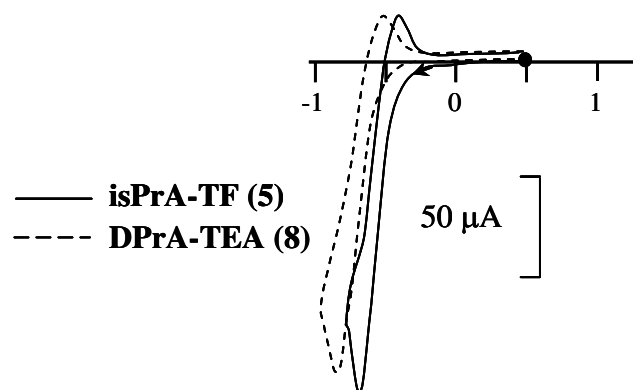


Figure 6

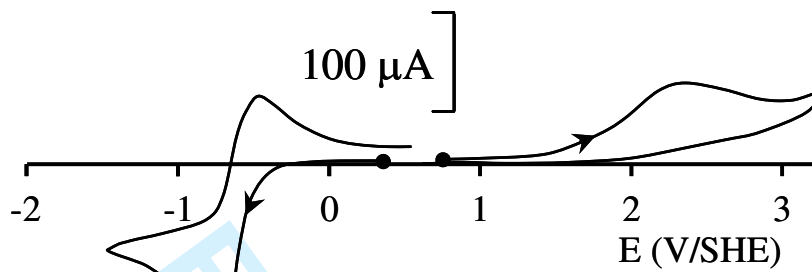


Figure 7

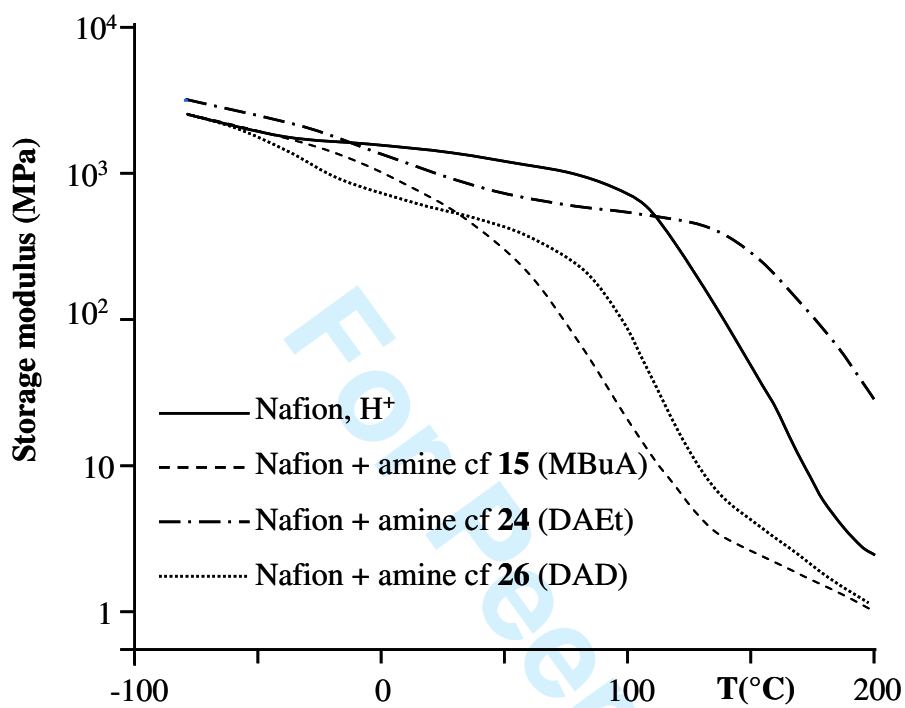


Figure 8.