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Anhydrous Proton Motion Study by Solid State NMR Spectroscopy in Novel PEMFC Blend Membranes Composed of Fluorinated Copolymer Bearing 1,2,4-triazole Functions and sPEEK.

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The proton mobility in a new family of PEMFC blend membranes containing 1,2,4-triazole groups is studied by infrared spectroscopy and particularly by ^{1}H Magic Angle Spinning Solid State NMR spectroscopy. These membranes are usually devoted for fuel cell operation at low relative humidity (RH < 25 %). The studied membrane contains 40 %-wt of a partially fluorinated alternating poly(2-iodoethyl vinyl ether–*alt*-chlorotrifluoroethylene)-*g*-1H-1,2,4-triazole-3-thiol$_{95\%}$ copolymer (II) and 60 %-wt of sulfonated poly(ether ether ketone), sulfonated PEEK (IEC = 1.3 meq.g^{-1}) (r = n_{-NH} / n_{-SO3H} = 1.7). In this study, the 1D ^{1}H MAS spectrum of copolymer (II) was fully attributed. Following acidification of a suspension of this copolymer leading to acidified (II') copolymer, the ^{1}D ^{1}H MAS spectrum showed two populations corresponding to triazole and triazolium groups respectively. The 2D ^{1}H EXchange SpectroscopY spectrum of (II') showed faster proton dynamics of the triazolium protonated form than in the copolymer containing only non protonated triazole groups. Inhomogeneity of (II') sample was confirmed by the different spin dynamics of triazole and triazolium ring protons. In the homogeneous membrane, spin dynamics were further increased (i.e. very short mixing time to observe proton diffusion). Hence, this work provides confirmation that protonation acts in favour of proton mobility in the material at room temperature, and provides experimental evidence for the increase of proton mobility due to triazole protonation from the sulfonic acid groups of sPEEK.

Introduction

Fuel cells are one of the most attractive approaches to energy conversion, due to their high flexibility and their easy handling. Indeed, fuel cells display a number of key advantages over conventional energy conversion devices, including low emissions and noise, flexibility in fuel selection, cogeneration capability and economy of scale [1]. In particular, the successful development of Proton Exchange Membrane Fuel Cells (PEMFCs) has generated widespread interest in these types of fuel cell potentially viable for automotive applications [2, 3]. However, the commercialization of PEMFC is still limited by high cost and unsatisfactory lifetime[4, 5] and mainly by hydrogen supply network development. Proton exchange membranes remain one of the most crucial components of such devices. Currently, the most commonly applied polymer membranes are based on perfluorosulfonic acid polymers (PFSA) such as Nafion ®, Flemion ®, Aquivion ®, Fumion ®, 3M ®, or Aciplex®. In the fully hydrated form, these membranes provide quite high proton conductivity of about 0.1 $S.cm^{-1}$ for RH > 75 – 80 % at a temperature below 100 °C for Nafion® [6, 7], which allows high power densities and efficiencies in fuel cell applications. However, proton conduction drops in Nafion® and related membranes when temperature is increased as liquid water evaporates from the membranes above 100°C at atmospheric pressure. High temperature operation of fuel cells offers several advantages [8] such as an increase of catalyst CO tolerance (at the anode), which simplifies hydrogen purification process [9], improved kinetics and reduced heat elimination issues [10].

To avoid demanding water management systems for fuel cell applications at temperatures above 100 °C [6, 11], a new class of proton conducting membranes is required, which do not rely on the diffusion of water (vehicle mechanism of proton conduction), the properties of which are independent of the overall degree of hydration of the membrane. Over the last decade, a new concept, pioneered by Kreuer [12] has evolved based upon alternative proton carriers to replace water as the proton solvent. The ideal protogenic group should be amphoteric, exhibit proton-donor and proton-acceptor properties, and show a high degree of self-dissociation [13]. It should also have a high dielectric constant to enhance the charge separation and be stable under fuel cell operation conditions. N-heterocycles [12, 14-17] behave as suitable proton-conducting species for immobilization onto a polymer backbone and, among them, imidazole [18-20], pyrazole [14], oxadiazole [21, 22], triazole [23-29], pyridine [30], and benzimidazole [28, 29, 31, 32] have been reported.

Triazole groups [28, 29, 33] are of particular interest as proton carriers for the development of membranes to be used in fuel cell applications. The basic nitrogen sites act as a proton-acceptor with respect to strong acid groups, such as sulfonic ($-SO_3H$) or phosphonic acid ($-P(=O)(OH)_2$). The rather isometric molecules are advantageous for extended local dynamics, and their protonated and non-protonated nitrogen atoms may behave as proton-donors and proton-acceptors in proton transfer reactions. Indeed, acid-doped N-heterocyclic-based [12, 14-17] systems may offer the possibility of suitable proton conductivity over a wide range of temperatures and particularly at high temperatures (120 – 200 °C) and the conductivity is expected to be less dependent on water content than in sulfonic acid functionalized materials.

We have recently described [28] a new family of proton conducting fluorinated copolymers grafted by azole functions (imidazole, benzimidazole or 1H-1,2,4-triazole) that was used in the preparation of blend membranes with sulfonated PEEK (sPEEK). Fluorinated polymers [34-38] are suitable candidates for high-temperature polymer electrolyte fuel cell [39] because of their remarkable thermal, and chemical properties and high oxidative stability [40]. This study investigated the influence of the nature of the N-heterocycle (i.e. imidazole, benzimidazole or 1H-1,2,4-triazole) on proton conduction and water uptake properties. Higher proton conductivity was observed for membranes containing pendant 1H-1,2,4-triazole functions. In addition, it was observed that an optimal r ratio ($r = n_{-Azole} / n_{-SO3H}$) was associated with the highest proton conductivity values and a minimum of activation energy for proton transport, which corresponded to an excess of azole compared to sulfonic acid functions brought by sPEEK. Further work that focused on triazole containing membranes showed that partial proton transfer occurred from sulfonic acid groups of sPEEK to the triazole groups [28].

To further investigate the proton motion in membranes based on copolymers containing 1H-1,2,4-triazole, it was of interest to apply two complementary spectroscopic methods: (i) infrared spectroscopy and (ii) ^1H Magic Angle Spinning (MAS) Solid State NMR spectroscopy. The former technique was used to highlight the protonation of triazole groups, while the latter provided evidence for the influence of the protonation of azole groups by the sulfonic acid functions on proton mobility in the final material.

^1H MAS NMR spectroscopy has been used previously to study proton conducting systems. For example, Bozkurt [41] used double-quantum 2D H MAS solid-state NMR spectroscopy to understand the proton exchange of a copolymer based on 1-vinyl-1,2,4-triazole and vinylphosphonic acid, but they did not characterize the copolymer by ^1H MAS NMR EXchange SpectroscopY (EXSY). Traer and Goward [42] characterized a model system comprising imidazole with three methyl phosphonate groups by ^1H MAS spectroscopy to highlight an example of cooperative ionic conductivity. Goward *et al.* [43] also reported 2D ^1H MAS NMR exchange spectroscopy (EXSY) spectra of telechelic oligomers bearing imidazole end-groups synthesized by Schuster *et al.* [15] doped by phosphoric acid. All of these studies were performed on model compounds that cannot be used as PEMFC membranes due to their hydro-solubility or that are not filmogenic materials. Only one study by Akbey *et al.* [44] has been carried out on polymer blend PEMFC membranes using 1D ^1H MAS, ^{13}C CP-MAS and 2D ^1H-^1H double-quantum MAS NMR spectroscopy. The purpose of the present article is to use 2D ^1H MAS NMR EXSY experiments on polymer blend PEMFC membranes to investigate proton motion. These experiments were carried at room temperature in order to observe slow motional process.

Experimental

Materials. *Tert*-butyl peroxypivalate (TBPPi, Trigonox 25- C75, 75 wt % solution in isododecane) was kindly provided by Akzo Nobel (Compiegne, France). Chlorotrifluoroethylene (CTFE) was supplied by Honeywell S.A. 1,1,1,3,3-pentafluorobutane ($C_4F_5H_5$) was kindly provided by Solvay S.A. (Brussels, Belgium). 2-Chloroethyl vinyl ether (CEVE), sodium iodide (NaI), potassium *tert*-butyl hydroxide (tBuOK), sodium hydroxide (NaOH), hydrochloric acid (HCl, 37%), potassium carbonate (K_2CO_3), acetone, dimethylsulfoxide, methanol, diethyl ether, dichloromethane, 4(5)-hydroxyethyl imidazole, 2-mercaptobenzimidazole and 1H-1,2,4-triazole-3-thiol were purchased from Sigma-Aldrich. Deuterated solvents (purity>99.8%) for liquid NMR were purchased from Euriso-top (Grenoble, France) Poly(ether ether ketone) (PEEK) was purchased from Goodfellow (Victrex® 450G, 80 µm powder). All reagents were used without further purification except for 1,1,1,3,3-pentafluorobutane and acetone which were distilled prior to use.

Characterization. Liquid NMR. Liquid Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AC 400 spectrometer, using deuterated dimethylsulfoxide or dimethylformamide as the solvent and tetramethylsilane (TMS) as the reference for ^1H nuclei. The experimental conditions for recording ^1H NMR spectra were as follows: flip angle 90°, acquisition time 3.9 s, recycle pulse delay 2 s, number of scans 128 and a pulse width of 5 µs for ^1H NMR, respectively.

Solid State NMR. Magic Angle Spinning (MAS) Solid State NMR spectra where recorded on a Varian VNMRS 600 spectrometer with a magnetic field strength of 14.1 T, at room temperature. A T3 triple resonance MAS probe HXY with a KelF stator and zirconia 1.2 mm o.d. pencil MAS rotor was used. The spectra were recorded at room temperature with a rotation speed of 55 kHz. For 1D spectra, a single pulse sequence was used. $\pi/2$ pulse duration was 2 µs and the recycle delay was set to 15 s. 16 transients were acquired. For 2D EXSY experiments, π/2 pulse duration was 2 µs, 3s recycle delay was used combined with a train of 60 presaturation pulses. 1, 10, 20, 35 and 50 ms mixing times were used to examine spin diffusion. A ^{1}H {^{14}N} HETero nuclear CORrelation experiment (HETCOR) used the Residual Dipolar Splitting interaction [45] to detect only protons close to ^{14}N. Spinning rate was 35kHz, π/2 pulse duration was 4 µs for ^{1}H, excitation and reconversion intervals $t_{exc} = t_{rec}$ were 450 ms, for ^{14}N the radiofrequency field strength was 40kHz and the lengths of the two ^{14}N pulses were τ_p = 22 ms. A unique delay Δt_1 of 2 rotors periods was used.

The isotropic chemical shift δ_{iso} was defined as

$$\delta_{iso} = \frac{1}{3}\left(\delta_{xx} + \delta_{yy} + \delta_{zz}\right) \text{ with } \delta_{ii} = \sigma_{ref} - \sigma_{ii}$$

and σ_{ii} (i=x, y, z) the principal components of the shielding tensor. The reference is the same as that used for liquid state NMR.

Gel Permeation Chromatography (GPC). Gel Permeation Chromatography (GPC) or Size Exclusion Chromatography (SEC) analysis was performed using a Spectra Physics Winner Station, a Waters Associate R 401 differential refractometer, and a set of four columns connected in series: Styragel (Waters) HR4 5 μm, HR3 analyses 5 μm, PL and Gel (Polymer Laboratories) 5 μ 100 Å. Monodispersed poly(methyl methacrylate) (PMMA) standards were used for calibration. Aliquots were sampled from the reaction medium, diluted with tetrahydrofuran up to a known concentration (Cp, t) ~ 2% wt. %, filtered through a 20 μm PTFE Chromafil Membrane, and finally analyzed by GPC at 30 °C, at a flow rate of 0.8 mL/min.

TGA. Thermogravimetric analyses (TGA) were performed in air with a Q50 apparatus from TA Instruments at a heating rate of 10 °C.min^{-1} from room temperature up to 800 °C. The sample size varied between 10 and 15 mg. For TGA analysis of blend membranes, an isothermal step at 160 °C for 20 min was first carried out to eliminate any residual solvent.

Proton conductivity. Membrane proton conductivities were determined from 2-electrode through-plane measurements using a Hewlett Packard HP4192A impedance meter. The samples were placed between two stainless steel electrodes of a closed conductivity cell that enabled regulation of temperature. Samples were allowed to equilibrate for 3 h at a given temperature prior to measurement. Conductivity values were determined from electrochemical impedance spectra acquired in the 10 MHz–100 Hz frequency range, using an amplitude of 100 mV. R was derived from the low frequency intercept of the low-frequency semicircle with the Re (Z) axis.

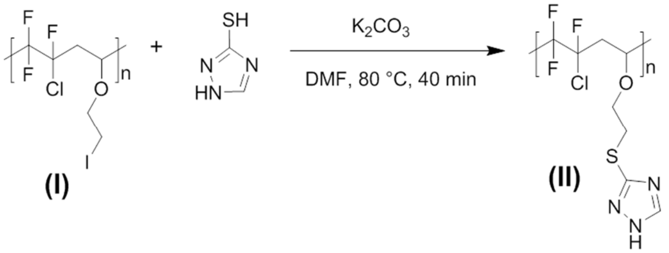
Synthesis of poly(CTFE-*alt*-CEVE) and poly(CTFE-*alt*-IEVE) (I) alternating copolymers. Published synthesis routes [46] were used to obtain the alternating poly(IEVE-*alt*-CTFE) copolymer with a iodine substitution degree ranging from 65 to 95 mol.%.

Grafting of 1H-1,2,4-triazole-3-thiol onto poly(IEVE-*alt*-CTFE) (I) alternating copolymer by nucleophilic substitution (II) (Scheme 1). In a three neck flask round bottomed, 2.32 g (22.98 mmol) of 1H-1,2,4-triazole-3-thiol and 3.17 g (22.98 mmol) of potassium carbonate were dissolved in 5 mL of dimethylformamide (DMF). The solution was heated at 80 °C with magnetic stirring for 1 h. Then, poly(IEVE-*alt*-CTFE) (I) copolymer (5.00 g) dissolved in DMF (5 mL) was added to the flask and the reaction was carried out at 80 °C under magnetic stirring for 20 min. The reaction mixture was then cooled to room temperature and the grafted copolymer was purified by precipitation from water to remove any unreacted 1H-1,2,4-triazole-3-thiol and potassium carbonate. The solid was separated by filtration, dried first under air flow for two days and then in a vacuum oven at 80 °C for 16 h. The degree of grafting was assessed by liquid ^{1}H NMR spectroscopy and reached c.a. 95 %-mol (poly(CTFE-*alt*-IEVE)-*g*-1,2,4-triazole-3-thiol$_{95\%}$) copolymer [28].

Liquid ^{1}H NMR (DMF-d^7, $(CD_3)_2NCOD$, ppm) δ: 8.4 (proton of the triazole ring, -C$\underline{\mathbf{H}}$,1H); 4.6 (CH_2-C$\underline{\mathbf{H}}$OR-CF_2, 1H); 4.1 (O-C$\underline{\mathbf{H_2}}$ -CH_2-Cl, 2H); 3.3 (O-CH_2 -C$\underline{\mathbf{H_2}}$-S-, 2H); 3.1 (traces) (O-CH_2 -C$\underline{\mathbf{H_2}}$-I, 2H) 2.5-3.2 (-CF_2-CFCl-C$\underline{\mathbf{H_2}}$-CHO-, 2H) .

Liquid ^{19}F NMR (DMF-d^7, $(CD_3)_2NCOD$, ppm) δ: -110 to -112, A part of AB system (-C$\underline{\mathbf{F_2}}$-CFCl-CH_2-CHO-, 1F); -114 to -116, B part of AB system (-C$\underline{\mathbf{F_2}}$-CFCl-CH_2-CHO-, 1F) ; -118, X part of ABX system (-CF_2-C$\underline{\mathbf{F}}$Cl-CH_2-CHO-, 1F); -120 (-C$\underline{\mathbf{F_2}}$-CFCl-CH_2-CHO-, 2F) [28].

Size Exclusion chromatography (SEC): M_n = 25,000 g.mol^{-1} (PMMA standards).



Scheme 1: Synthesis of poly(CTFE-*alt*-IEVE)-*g*-1H-1,2,4-triazole-3-thiol copolymer (II) by grafting of 1H-1,2,4-triazole-3-thiol onto poly(CTFE-*alt*-IEVE) copolymer (I).

Sulfonation of poly(ether ether ketone) (PEEK). In a 100 mL round bottomed flask equipped with a mechanical stirrer, 5.00 g of PEEK and 49 mL of sulfuric acid (96-97 %) were introduced. The reaction was carried out at 25 °C, under magnetic stirring (50 rpm) for 66 h. The sulfonation reaction was quenched by pouring the mixture into deionized water (18 mQ), enabling sPEEK to precipitate as fine white strands. These strands were then washed with deionized water several times until the pH of the eluent water reached 7.0, and were dried under vacuum at 50 °C to constant weight. The degree of sulfonation and ion exchange capacity (IEC) of sPEEK was determined by liquid ^{1}H NMR spectroscopy, elemental analysis and acid-base titration [47-52].

Membrane preparation. Poly(IEVE-*alt*-CTFE)-*g*-1H-1,2,4-triazole-3-thiol$_{95\%}$ (II) copolymer was dissolved in DMSO (30 wt %) to which a few drops of aqueous lithium chloride (3 mol.L^{-1}) were added to improve solubility. The solution was magnetically stirred and heated at 120 °C for 1 h. A DMSO solution (15 wt %) of sPEEK was prepared similarly. The polymer solution was slowly added to the sPEEK solution under strong stirring, heated at 120 °C to yield a dark brown solution, and then sonicated for 3 h. The solution was filtered to separate any insoluble materials and then it was cast onto a glass plate with a doctor blade. The cast film was then transferred to a vacuum oven, where solvents were evaporated by the following heating cycle: first, it was dried at 80 °C under vacuum for 12 h and then at 120 °C for 4 h under vacuum to evaporate any residual solvent. The resulting membranes were removed from the glass substrate by immersion in either deionized water or aqueous hydrochloric acid (1 mol.L^{-1}), when the acid form membrane could be recovered directly. Any residual solvent and lithium ions [53] were eliminated by carefully washing the membrane in HCl (1 mol. L^{-1}) at 90 °C for 2 h, then in deionized water at 90 °C for 2 h.

Results and discussion

Synthesis, thermal and structural analyses of polymer blends.

Poly(IEVE-*alt*-CTFE)-*g*-1H-1,2,4-triazole-3-thiol$_{95\%}$ copolymer (II) / sPEEK blends have shown conductivities of ca. 7 mS.cm^{-1} at 140 °C, RH < 25 % [28] for r = 1.7. Different azole-grafted fluorinated copolymers / sPEEK weight ratios were used to investigate the influence of the basic: acid sites ratio, named r = n_{-NH} / n_{-SO3H}. Through-plane proton conductivity was determined in a two-electrode cell as a function of temperature at low relative humidity (RH < 25 %) [28] and it was observed that membranes exhibited an Arrhenius-type dependence from 40 to 140 °C [28]. Membranes are denoted M3: (II) (X) / sPEEK (Y), where X and Y are the mass percentages of copolymer(II) and sPEEK in the membrane, respectively. Figure 2 represents the proton conductivity, plotted against reciprocal temperature, of the most highly proton conducting membrane (i.e. r = 1.7). These results showed that the blend membranes exhibited higher proton conductivity than the copolymer (II) (r = ∞) and sPEEK membrane (r = 0) in these conditions (Figure 2).

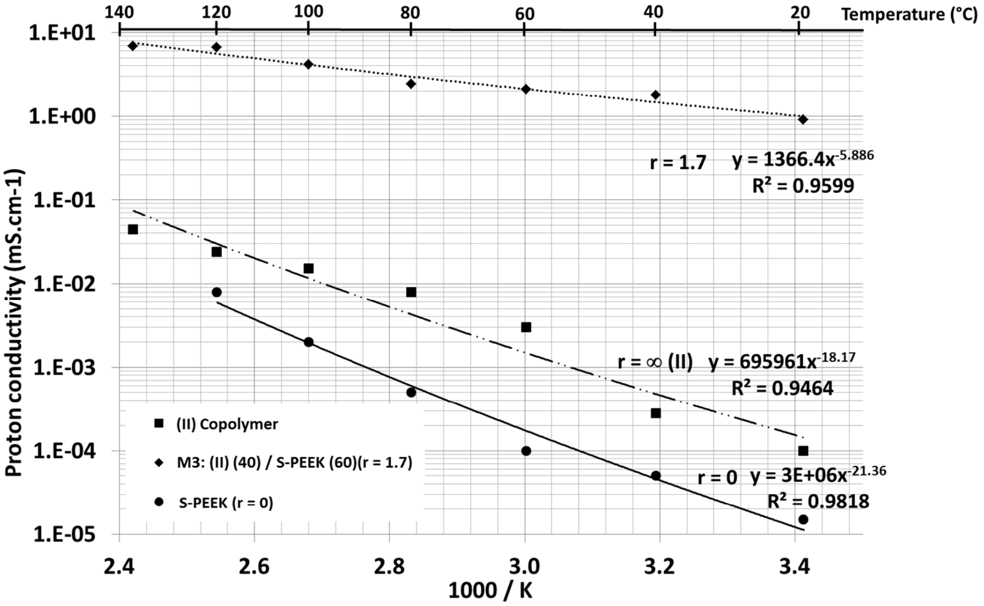


Figure 2: Dependence of proton conductivity on reciprocal temperature of copolymer (II), M3: (II) (40) / sPEEK (60) (r = 1.7) and sPEEK membranes, with RH < 25 %. Proton conductivity of Nafion® membrane (reference for T < 120 °C): 3.1 x 10^{-1} and 4.0 x 10^{-1} mS.cm^{-1} at 140 and 120 °C, respectively (RH < 25 %) [54]. Proton conductivity of Celtec® BASF membrane (PBI doped H_3PO_4; reference for T > 140 °C): 4.7 mS.cm^{-1} at 150 °C, RH = 5 % [55].

M3: III (40) / sPEEK (60) (r = 1.7), named M3-A, exhibited higher proton conductivity.

Infrared spectroscopy (FTIR). Figure 3 exhibits the FTIR spectra of M3-A, sPEEK membrane and the poly(IEVE-*alt*-CTFE)-*g*-1H-1,2,4-triazole-3-thiol$_{95\%}$ (II) copolymer. That of sPEEK displays a band at 1590 cm^{-1} corresponding to the C=O stretching vibration while the broad absorption band between 1080 and 1320 cm^{-1} is attributed to the ether C-O vibration of sPEEK. The characteristic bands at 1000 and 1070 cm^{-1} correspond to $-SO_3H$ stretching vibrations and the broad band centred at 3450 cm^{-1} is assigned to O-H stretching vibrations from water adsorbed by sPEEK. Although the sPEEK membrane was dried before FTIR measurements, some water was still absorbed by the hygroscopic sulfonic acid functions. Figure 3 shows that this broad band assigned to water absorbed is more intense in sPEEK than in M3-A membrane. Indeed, when sPEEK is blended with copolymer (II), the sulfonic acid functions of sPEEK induce acid/base interactions with triazole groups, and the quantity of absorbed water is lower. Bands at 1400, 1460 and 1470 cm^{-1} are attributed to the aromatic ring skeletal vibrations. The FTIR spectrum of poly(CTFE-*alt*-IEVE)-*g*-1H-1,2,4-triazole-3-thiol$_{95\%}$ copolymer (II) displays an overlapping of absorption bands from 1020 to 1160 cm^{-1} assigned to C-F and C-O stretching vibrations. The bands centred at 2890 and 3030 cm^{-1} are assigned to the –N-H stretching of the triazole groups. In the M3-A membrane the υ_{-NH} bands are weak, in agreement with the low mass percentage of copolymer (II) in the membrane (40 wt% of copolymer (II) M3-A membrane).

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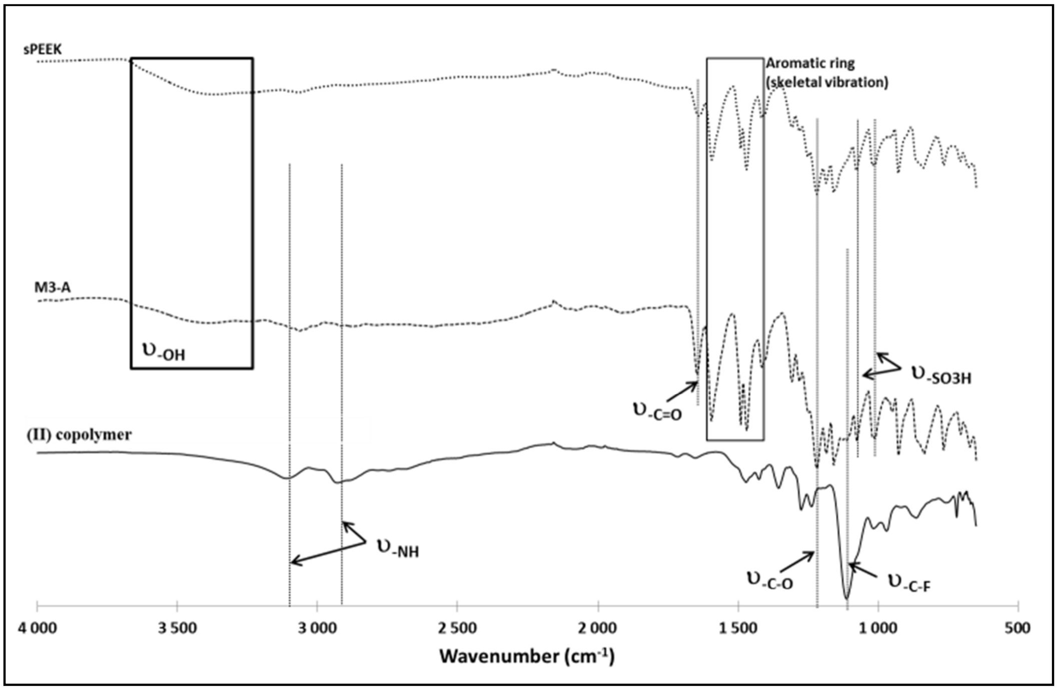

Figure 3: FTIR spectra of poly(CTFE-*alt*-IEVE)-*g*-1H-1,2,4-triazole-3-thiol$_{95\%}$ copolymer (II), M3-A (medium), s-PEEK membranes, at 20 °C.

Identification of 1D single pulse ^{1}H MAS lines The synthesis of copolymer (II) was reported in a previous study [28]. Liquid state ^{1}H NMR spectroscopy (Figure SI1 in the supporting information) allowed calculation of the degree of grafting of 1H-1,2,4-triazole-3-thiol as ca. 95%-mol onto the fluorinated poly(CTFE-*alt*-IEVE) copolymer (I) [28]. However, the –NH group of the grafted 1H-1,2,4-triazole-thiol was not clearly evidenced by liquid ^{1}H NMR due to exchange with the DMSO solvent. To tackle this issue, poly(IEVE-*alt*-CTFE)-g-1H-1,2,4-triazole-3-thiol$_{95\%}$ copolymer (II) was analyzed by ^{1}H MAS NMR spectroscopy and Figure 4 a) represents the single pulse ^{1}H MAS NMR spectrum. It exhibits three main signals. From the liquid NMR spectrum, the broad band with chemical shift between -1 and 6 ppm is attributed to i, j, k and l protons of the partially fluorinated copolymer main chain (i and j in Figure 4 a) and Figure SI1) and to the four protons in -O–C**$\underline{H_2}$**-C**$\underline{H_2}$**-S- group (k and l in Figure 4 a) and Figure SI1). This assignment was confirmed by recording the ^{1}H MAS NMR spectrum of poly(CTFE-*alt*-IEVE) copolymer (I) (i', j',k' and l' in Figure SI2) and was in good agreement with that of liquid spectrum of these poly(CTFE-*alt*-IEVE) (I) copolymers (i', j', k' and l' in Figure SI3).

1H-1,2,4-triazole-3-thiol ^{1}H MAS NMR spectrum of Figure 5 a) displays a peak centred at 8.5 ppm, which is assigned to m proton of the triazole ring as in the liquid state. In order to identify q proton linked to the nitrogen atom (not observed from liquid state NMR) in the triazole ring (–N**H_q**), a HETCOR experiment between ^{1}H and ^{14}N nuclei was recorded, Figure 5 b), which indicates that the signal at 13.8 ppm corresponds to the closest proton to nitrogen. This signal can thus be unambiguously attributed to q protons. Finally, the signal at 12 ppm in Figure 5 a) can be attributed to r protons linked to the sulfur atom. As expected, this signal is not present in the spectrum of the poly(IEVE-*alt*-CTFE)-*g*-1H-1,2,4-triazole-3-thiol$_{95\%}$ (II) copolymer (Figure 4 a). ^{1}H MAS NMR spectroscopy therefore enables identification of the proton linked to the nitrogen atom in the triazole ring (-N**H**).

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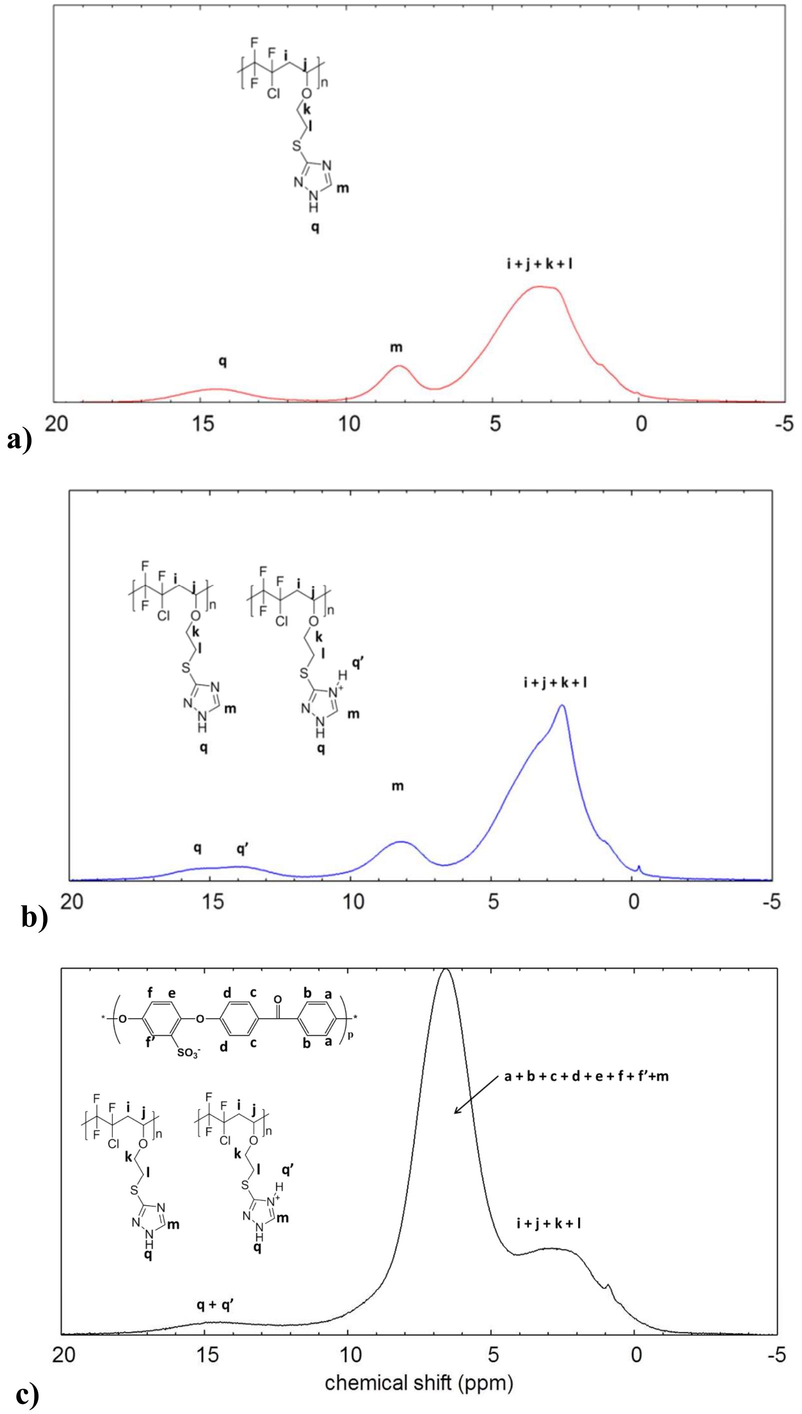

Figure 4: 1D single pulse ^{1}H MAS SSNMR spectra of poly(CTFE-*alt*-IEVE)-*g*-1H-1,2,4-triazole-3-thiol$_{95\%}$ (II) (a), poly(CTFE-*alt*-IEVE)-*g*-1H-1,2,4-triazole-3-thiol$_{95\%}$ partially protonated by hydrochloric acid (II') (b) and of M4-A membrane (40 %-wt (II) copolymer / 60 % sPEEK) (c), at 20 °C. These three spectra were normalized with respect to the signal at 13.8 ppm.

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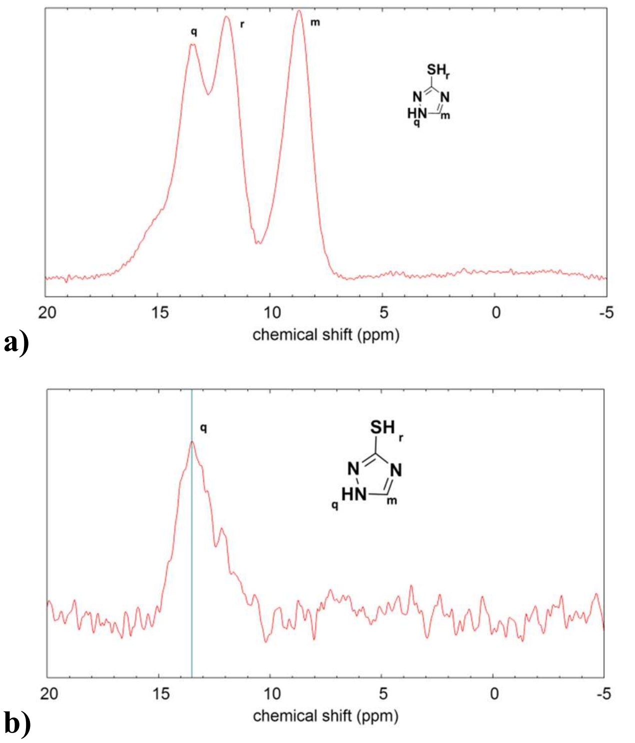

Figure 5: a) Single pulse ^{1}H MAS SSNMR spectrum of 1H-1,2,4-triazole-3-thiol. b) HETero nuclear CORelation (HETCOR) SSNMR spectroscopy experiment between ^{1}H and ^{14}N nuclei on 1H-1,2,4-triazole-3-thiol, at 20 °C.

Poly(IEVE-*alt*-CTFE)-*g*-1H-1,2,4-triazole-3-thiol$_{95\%}$ (II) copolymer was then acidified by a concentrated solution of hydrochloric acid (HCl 8 mol.L^{-1}) for 16 h, at room temperature to partially protonate the triazole rings (pK$_{a1}$ = 10.3 [56]). The protonation is evidenced by a change in color from dark green for the unprotonated (II) copolymer to orange for the protonated triazolium form, noted (II') below. The ^{1}H MAS NMR spectrum of this partially protonated copolymer (II') bearing both triazole and triazolium functions is displayed in Figure 4 b). As all subsequent ^{1}H spectra, it was normalized with respect to the signal centred at 13.8 ppm (Figure 4 a). It displays the same signals noted (i, j, k, l), m and q at around 15.5 ppm as for non protonated (II) copolymer while a new peak at 13.8 ppm is assigned to the q' proton linked to the azolium rings. To obtain this triazolium form, the copolymer (II) was washed with aqueous HCl, which probably eliminates short polymer chains, which decreases the polydispersity index. On the one hand, this washing must explain why the signal that corresponds to (i; j; k; l; l) group of the protonated (II') copolymer has a different shape and is narrower than that of the unprotonated (II) copolymer. On the other hand, the peak assigned to the m proton of the triazole group of the protonated (II') copolymer is broader than that of the unprotonated (II) copolymer. This may arise from the presence of triazole and triazolium in (II') copolymer, which enlarges the peak corresponding to the m proton due to the increase of dipolar interaction and isotropic chemical shift distribution in (II') copolymer. The procedure used to acidify poly(IEVE-*alt*-CTFE)-*g*-1H-1,2,4-triazole-3-thiol$_{95\%}$ (II) copolymer explains the partial protonation of the triazole groups. Indeed, this protonation was carried out on a dispersion of poly(IEVE-*alt*-CTFE)-*g*-1H-1,2,4-triazole-3-thiol$_{95\%}$ (II) in HCl, which means that only the copolymer at the interface with the acid has been protonated. The two distinguishable peaks corresponding to q and q' protons indicate the non homogeneity of the (II') copolymer.

sPEEK was also characterized by single pulse ^{1}H MAS solid-state NMR spectroscopy where a broad main signal centred at 6.4 ppm assigned to the aromatic protons is observed while the peak corresponding to the proton of the sulfonic acid group (observed at 7.5 ppm) is in good agreement with Paik *et al.*'s results [57] (Figure SI4 in the supporting information).

Figure 4 c) represents the single pulse ^{1}H MAS NMR spectrum of M3-A membrane with a (II) copolymer: sPEEK composition of ca. 40 %-wt and ca. 60 %-wt (r = 1.7). This spectrum displays a broad peak ranging between -1.0 and 4.5 ppm attributed to (i; j; k and l) protons of copolymer (II). The broad signal centered at 7 ppm is attributed to all the aromatic protons of sPEEK and the proton m (-C**H$_m$** from the triazole ring) overlapped with this broad peak ranging from 5.0 to 9.0 ppm. The peak, corresponding to the sulfonic acid proton (-SO$_3$H) of sPEEK at 8 ppm, is not present in the M3-A membrane spectra in contrast to that noted in the ^{1}H MAS solid-state NMR spectrum of s-PEEK (Figure SI4). This clearly indicates that sulfonic acid function is under its ionic form (sulfonate form -SO$_3^-$). Consequently, the acid proton of the sulfonic function (pK$_a$ < 0) has been transferred onto the triazole pendant groups (in excess) (r = 1.7) *via* an acid / base exchange (pK$_{a\ 1,2,4\text{-triazole}}$ = 10.3). It is observed that the overlapped peak corresponding to unprotonated (q proton) and protonated triazole groups (q' proton) has a low intensity in agreement to the low triazole concentration in M3-A polymer blend (ca. 40 %-wt of (III) copolymer). The presence of both overlapped peaks means that triazole groups were protonated by sulfonic acid (strong acid) of sPEEK. Because of the excess of triazole groups (r = 1.7) compared to the sulfonic acid functions, a part of these triazole functions have not been protonated. However, the broad overlapped peak corresponding to both q and q' proton reveal an intermediate or fast exchange[58] of the excess of proton between triazole and triazolium groups (i.e. equilibrium between triazole and triazolium forms).

^{1}H spin diffusion studied by 2D EXSY. ^{1}H MAS NMR EXSY spectra enabled further study of the proton dynamics in slow exchange regime [58]. During this pulse sequence transverse ^{1}H magnetization is first built that evolves under the chemical shift interaction during t$_1$. It is then stored along the static magnetic field B$_0$ during the variable exchange/mixing time t$_{mix}$ while ^{1}H spin diffusion could occur. The last pulse allowed detection of ^{1}H free induction decay during t$_2$ (Figure 6). After Fourier transform, off diagonal peaks enabled detection of ^{1}H spins that jump from one site to another one in a slow exchange regime [58]. Diagonal peaks, also named auto-correlation peaks, evidence ^{1}H spins that remain in the same position or jump in a similar site associated to the same chemical shift. In this work, we will focus on the behaviour of the intensity of the off diagonal peaks as well as of the auto-correlation peaks with the mixing time in fewer samples where proton mobility will vary. For the same value of t_{mix}, a higher intensity of a off diagonal peak indicates a higher mobility. This should be also associated to a lower intensity for the corresponding auto-correlation peak of the starting point.

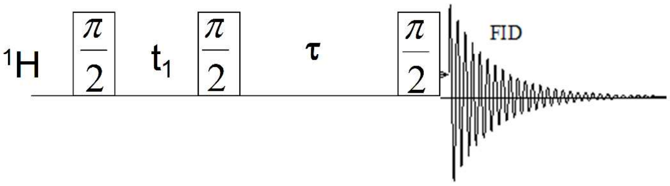

Figure 6: EXchange SpectroscopY (EXSY) pulse sequence.

Experiments were performed on (II) copolymer and on the partially protonated form (II’), using different mixing times t_{mix} = 1, 10, 20, 35, and 50 ms. The aim of these measurements is to observe the effect of the partial protonation of azolium groups on the proton mobility. Figure 7 displays five ^{1}H MAS NMR EXSY spectra of (II) copolymer. It is observed that for t_{mix} = 1ms mainly auto-correlation peaks are observed along the diagonal. That means that the mixing time of the EXSY sequence is too short so that efficient spin diffusion cannot occur for all protons (i.e. protons remain on their initial position after t_{mix}). The broad shape of these auto-correlation peaks is explained by the flexibility of the ether and thio-ether linkage of the pendant group that bears the triazole function (Scheme 1 and Figures 7-9). For t_{mix} = 10 ms, first exchange between (i; j; k; l) protons and m protons belonging to the triazole group is observed, probably enhanced by spatial proximity. This proton exchange can be the consequence of an intra-chain or extra-chain exchange. For $t_{mix} \geq 20$ ms, mixing times of the EXSY sequence are long enough to enable spin diffusion between q protons of the –N**H** of the triazole group and (i; j; k; l) protons. For t_{mix} = 50 ms (e), the correlation peaks intensity indicates that exchange between q protons of the –NH group of the triazole function is more in favor of (i; j; k; l) protons than of m protons. For t_{mix} = 50 ms (e), the intensity of the auto-correlation peak of q proton is slightly reduced, but a majority of them remain on their initial position. This can be the consequence of probable interactions between triazole groups (hydrogen bonds) that restrain the mobility of these protons. Some of these q protons (not involved in triazole groups interactions) are moving to (i, j, k and l) site mainly enhanced by the spatial proximity and the flexibility of thio-ether and ether linkages of (II) copolymer.

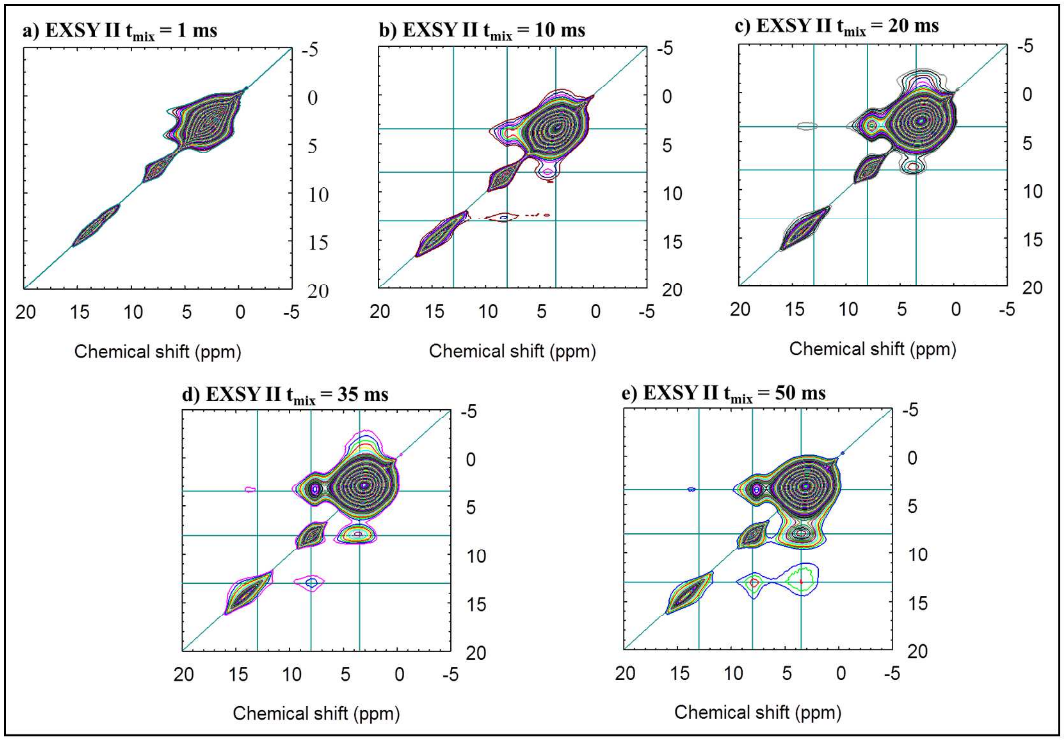

Figure 7: ^{1}H MAS solid-state NMR EXchange SpectroscopY spectra of (II) copolymer with t_{mix} = 1 ms (a), t_{mix} = 10 ms (b), t_{mix} = 20 ms (c), t_{mix} = 35 ms (d) and t_{mix} = 50 ms (e) at 20 °C.

Figure 8 shows the ^{1}H MAS NMR EXSY spectra of the (II’) protonated copolymer. Two populations (q and q’ protons) can be clearly distinguished in the 13 to 16 ppm-range. The first exchange is observed for m and q’ protons with the other protons of the grafted fluorinated copolymer is noted for much shorter mixing time i.e. t_{mix} = 10ms (Figure 8 b) than for non-protonated (II) copolymer. This result showed that q’ protons of triazolium groups are more mobile than q protons of triazole groups. This result is direct evidence that the protonation of triazole pendant groups greatly favours mobility and hence proton transfer, and proton conduction of copolymer (II). Moreover, for the large t_{mix} = 50ms (e), the auto-correlation peak intensity of q’ proton is severely reduced and only an auto-correlation peak corresponding to q proton is observed.

That means that for t_{mix} = 50ms (e), q' protons had enough time (mixing time) to shift to another site, i.e. the probability that the q' proton remains on the q' site is close to zero. However, a significant amount of q protons, which are less mobile than q' protons, stay in their sites, even when t_{mix} = 50 ms (e). As mentioned above, the coexistence of protonated and non-protonated triazole pendant groups is explained by the acidification process, i.e. suspension in acid solution.

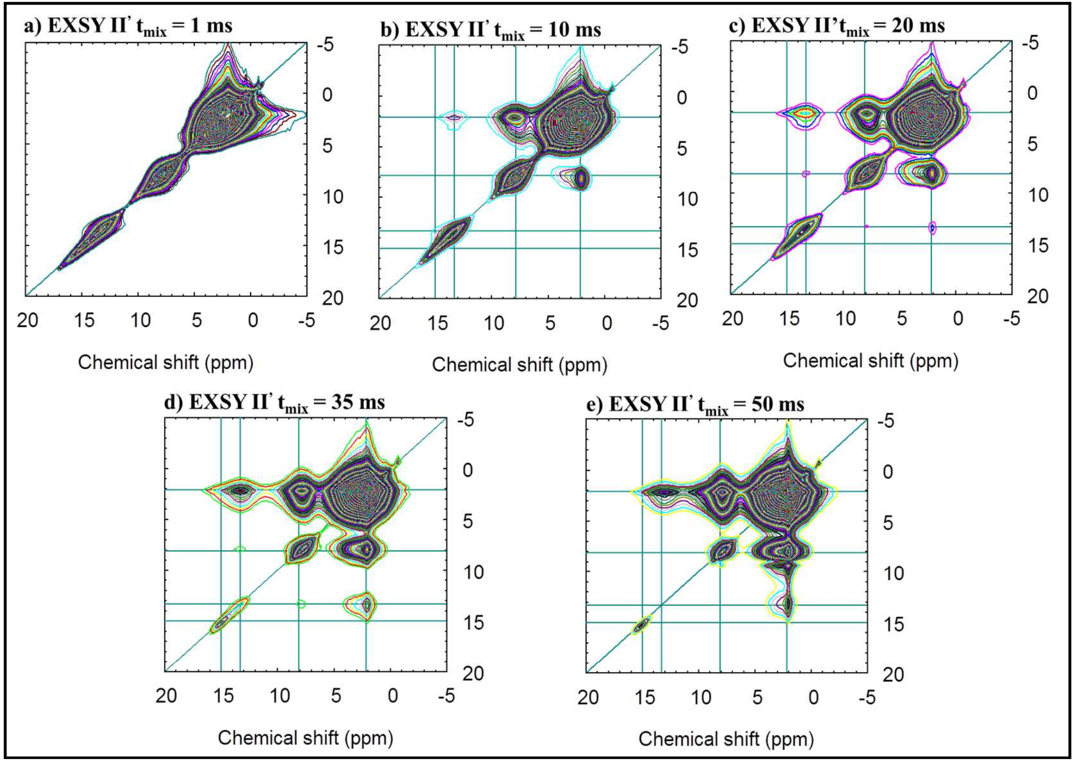
a) EXSY II' t_{mix} = 1 ms
b) EXSY II' t_{mix} = 10 ms
c) EXSY II' t_{mix} = 20 ms
d) EXSY II' t_{mix} = 35 ms
e) EXSY II' t_{mix} = 50 ms

Figure 8: ^{1}H MAS solid-state NMR EXchange SpectroscopY spectra of protonated by HCl (II$'$) copolymer with t_{mix} = 1 ms (a), 10 ms (b), 20 ms (c), 35 ms (d) and 50 ms (e), at 20 °C.

^{1}H MAS NMR EXSY spectrum of M4-A membrane (Figure 9) shows only one average population assigned to q and q' protons observed at ca. 14.3 ppm. This first result provides evidence that a significant proportion of the triazole groups of the fluorinated copolymer have been protonated by sulfonic acid functions of sPEEK. This is explained by both the strong acidity of sulfonic acid functions of sPEEK and the processing of membrane. M3-A membrane was prepared by dissolving both (II) copolymer and sPEEK until a clear solution was observed, i.e. both polymers were totally dissolved, which acted in favour of acid-base exchange between triazole groups of the fluorinated copolymer and sulfonic acid functions in sPEEK. Due to this process, triazole and triazolium had time to organize together in order to create a fast mobility of the excess of proton between these triazole and triazolium form (i.e. equilibrium between triazole and triazolium forms). As a consequence, proton spin diffusion of the q' and q protons average corresponding peak is observed for t_{mix} = 1 ms, i.e. for an extremely short mixing time compared to (II$'$) acidified copolymer. This indicated a good homogeneity in the M3-A membrane sample.

As observed with ^{1}H MAS solid state NMR EXSY spectroscopy of protonated (II$'$) copolymer, the auto-correlation peak intensity of signals corresponding to q' protons decreases when t_{mix} increases. As discussed above, proton mobility of q' proton started for t_{mix} = 1 ms (a), and the auto-correlation peak corresponding to q' protons completely varnished for t_{mix} = 50 ms (d). The off-diagonal correlation peaks with the large signal centred at around 7 ppm mean that they can be transferred onto the m sites or onto the aromatic ring protons of sPEEK. The exchange observed between the (i, j, k and l) protons and the intense peak centered at 7 ppm confirms a suitable blend obtained between (II) copolymer and sPEEK.

^{1}H MAS NMR EXSY spectroscopy displayed that the protonation of triazole pendant groups of the partially fluorinated copolymer (II) increases triazole proton mobility. Acid-base interactions allowed protonatation of triazole pendant groups, thus creating protonated triazolium groups bearing q' protons.

This study demonstrated that q' protons are more mobile than q protons (corresponding to non-protonated triazole groups). This NMR spectroscopic study allowed us demonstrating that: (i) on the one hand, all the acidic protons of the sulfonic acid functions of sPEEK are transferred onto the basic triazole groups (n > 1) *via* acid / base exchanges, and (ii) on the other hand, the presence of protonated triazole group (triazolium form) increases the proton mobility in the membrane (as demonstrated by numeric simulation for imidazole salt by Munch et *al.* [59]).

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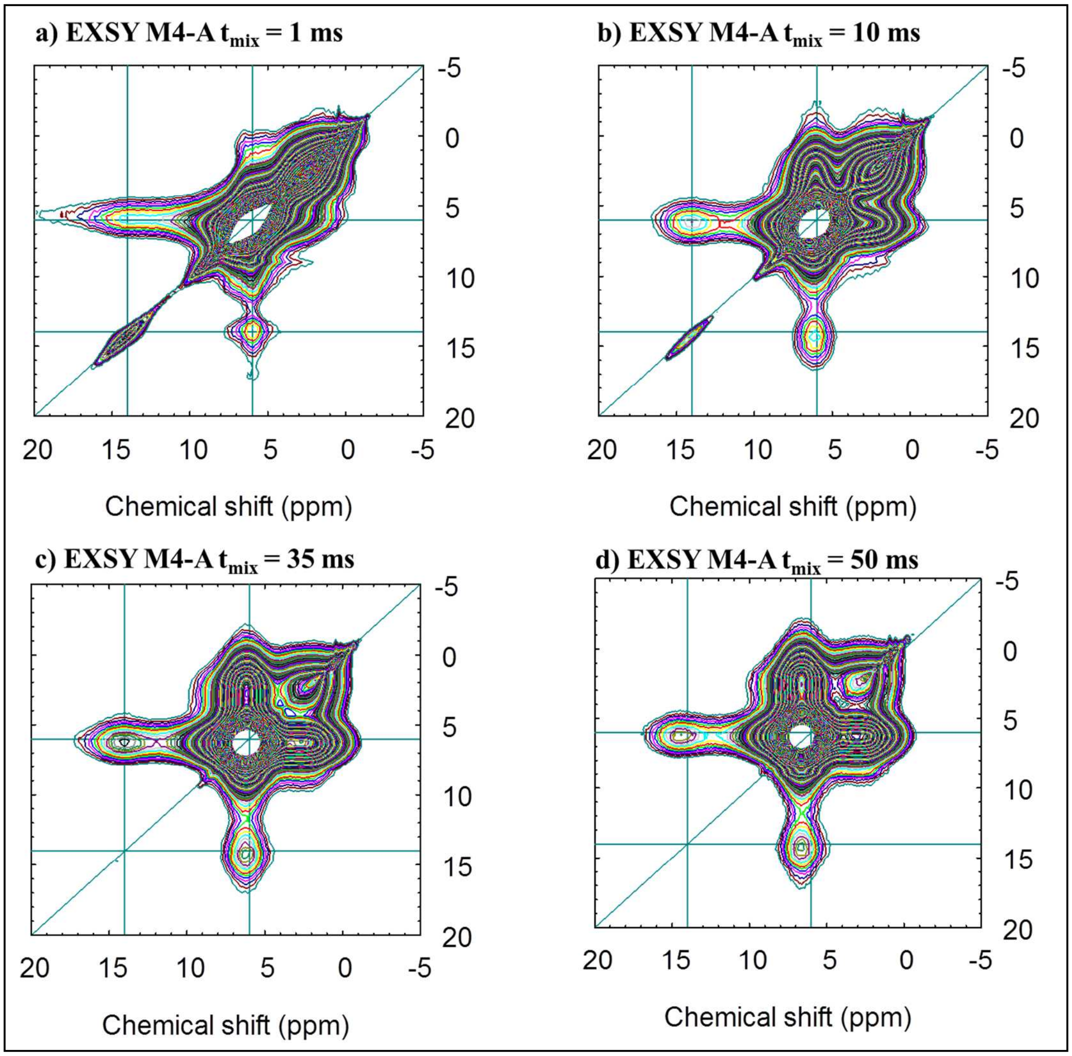

Figure 9: ^{1}H MAS SSNMR EXchange SpectroscopY spectra of M4-A membrane (40 %-wt (II) copolymer / 60 % s-PEEK) with t_{mix} = 1 ms (a), 10 ms (b), 35 ms (c) and 50 ms (d), at 20 °C.

Conclusions

1D ^{1}H MAS spectrum of (II) copolymer was fully attributed and allowed observation of the proton site of the secondary amine function of the triazole ring site at 13.8 ppm (not observed in liquid state NMR). In its partially protonated triazolium form, a specific line was observed at 15.5 ppm in (II') copolymer together with the line at 13.8 ppm indicating that protonation is not homogeneous in the sample due to the acidification process (i.e. suspension of (II) copolymer in HCl). In membrane M3-A the SO_3H group protons were no longer observed, which indicates complete transfer of this proton from sPEEK to the copolymer. Only one line corresponding to triazolium form is observed indicating homogeneous blend of copolymer II and s-PEEK together with fast proton exchange between triazolium and triazole rings.

2D ^{1}H EXSY spectra of copolymer II showed that an intra-chain slow regime exchange of protons is observed for $t_{mix} \geq$ 20ms. Under its protonated form proton mobility was increased and exchange was observed since $t_{mix} \geq$ 10 ms ; inhomogeneity of sample protonation was confirmed by different spin dynamics of triazolium and triazole rings protons. In M3-A membrane proton mobility was further increased and exchange was observed since t_{mix} = 1ms. Even more for $t_{mix} \geq$ 35 ms all triazolium protons have switched to another position.

Hence this work highlights that protonation of triazole groups acts in favour of proton mobility within the PEMFC membranes at room temperature. Increase of proton mobility due to triazole protonation by sPEEK had thus been proved. Deeper understanding of the mechanism of proton transport in the membranes will be studied by varying sample temperatures in order to influence fast exchange dynamics.

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Notes and references

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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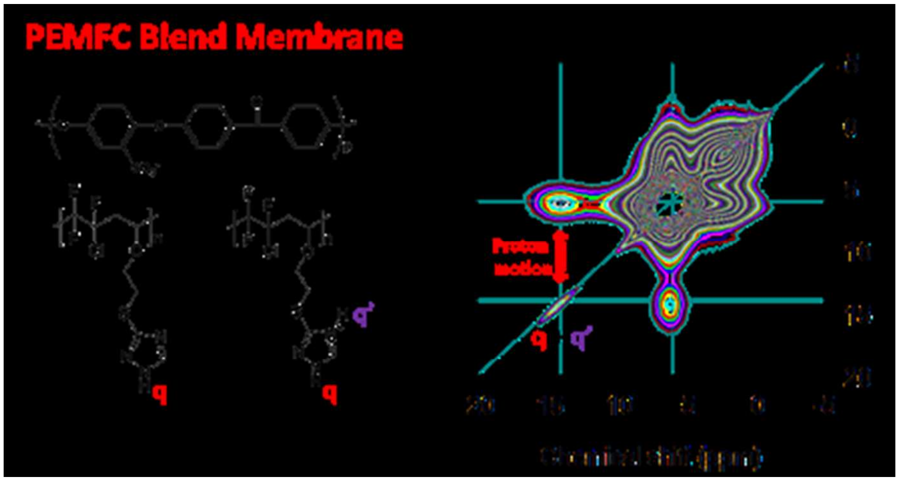

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