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Polyalkylphosphazenes as solid proton conducting electrolytes

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Several polydialkylphosphazenes, $[P(R'R'')=N]_n$, R′ and R″ = Me, Et, Pr; Bu, hexyl, were considered for the fabrication of solid proton conducting electrolytes due to their capacity to be protonated at the chain N atom. Protonated polydipropylphosphazene ($PDPrP{\cdot}nH^+$) was found the most suitable to this purpose. The solid state proton conducting properties and structural stability of $PDPrP{\cdot}nH^+$ at $1H_3PO_4/N$ mole ratio in composite materials with polyphenylensulfide (Ryton®) were studied by conductivity measurements in the 29–79°C temperature (*T*) and 0–33% relative humidity (RH) ranges, and by thermal analysis and NMR spectroscopy. The conductivity was found to increase upon increasing *T* and RH. Conductivity at 33% RH was in the same range of values reported for other polymers containing sulphonic or phosphonic acid groups. Conductivity in the dry state was in the range of values reported for polymers containing imidazole rings. NMR and conductivity data showed that upon aging in the above experimental conditions the polymer undergoes structural changes and exhibits higher conductivity.

1. Introduction

One of the most important applications of solid proton conductors is their use as electrolytes in fuel cells operating at low temperatures (<100°C). A further significant improvement is the extension of the cell operating temperature to medium values (120–160°C). The achievement of such an aim is challenging and it needs the development of proton conductor membranes able to work in dry or low humidity environments [1].

Strong acid systems based on H_3PO_4 [2] or acid organic polymers containing $-SO_3H$ and $-PO_3H_2$ functional groups [3–5] have been considered first as proton conducting electrolytes. They exhibit good proton conductivity ($\sigma = 10^{-2}$–10^{-1} S cm^{-1}) at high RH values. Water in these systems has the role to generate protonated sites with hydrogen bonds allowing the proton transfer through the solid electrolyte and to inhibit the loss of active protons. Operating with high water pressure values is necessary in order to have the same performances at medium temperatures. Therefore, an acceptable compromise between water pressure and proton conductivity must be found experimentally for each material.

To overcome this limitation, polymers containing imidazole [3, 6–8] or imine [9] rings, protonated by H_3PO_4, have been suggested as possible proton conductors in dry conditions. Protons may transfer through phosphate ions in such systems. In this context, polydialkylphosphazenes, $[P(R'R'')=N]_n$, seemed to us worth to be investigated for their capacity to be protonated [10].

Polyphosphazenes are indeed very versatile polymers. Polydialkylphosphazenes are basic polymers whereas polydiaryloxyphosphazenes can be functionalised to yield acid polymers. A great variety of polyaryloxyphosphazenes was synthesized [11]. Sulfonated poly [bis(phenoxy)]phosphazenes were first obtained by Montoneri *et al.* [12, 13]. These polymers, at high degree of sulfonation, are water soluble and therefore not suitable to perform as solid electrolytes in aqueous

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environment. Afterwards, other workers obtained and tested water insoluble crosslinked sulfonated and phosphonated polyphosphazenes [4, 5] as solid polymer electrolytes.

By comparison the number of synthesized polydialkylphosphazenes is limited to a few substituents, i.e., $[P(R'R'')=N]_n$ with R′ and/or R″ = Me [10, 14, 15], Et [10, 15, 16], Pr [16, 17], Bu and hexyl [15]. The nature of the alkyl substituents strongly affects the product yield, the polymer molecular weights and the physical-chemistry properties. Preliminary screening investigation indicated polydipropylphosphazenes (PDPrP) as the most suitable polydialkylphosphazene to obtain solid proton conducting electrolytes.

Polydimethylphosphazene was discarded due to its solubility in water when protonated. Polydiethylphosphazene is insoluble in water, however skeletal bonds cleavage has been reported upon aging in acid solution [10]. The phosphazenes with alkyl substituents longer than Pr were obtained in very low yield and/or low molecular weights. Hereinafter, only the results obtained with PDPrP are reported.

2. Experimental

2.1. Polymer synthesis and characterization

PDPrP was synthesized according to the reaction:

$$n\mathrm{Me_3SiN} = \mathrm{P(Pr)_2OCH_2CF_3} \rightarrow [\mathrm{P(Pr)_2} = \mathrm{N}]_n + n\mathrm{Me_3SiOCH_2CF_3}$$

This reaction was performed in sealed glass vials at 190°C as previously reported [17].

The preparation of protonated polydipropylphosphazene ($PDPrP{\cdot}nH^+$) was accomplished by dissolving PDPrP in 99% HCOOH at 0.5 g/ml concentration and then adding to the solution 85% aqueous H_3PO_4 at 0.5–3 H_3PO_4/N mole ratio. The protonated polymer could be recovered as solid material by solvent vacuum evaporation. Both PDPrP and ($PDPrP{\cdot}nH^+$) were characterized by ^{31}P NMR, IR and X-ray spectroscopy, and by thermal analysis.

2.2. Fabrication of solid electrolytes

For the fabrication of the solid electrolytes membrane, a solution of $PDPrP{\cdot}nH^+$ at $1H_3PO_4$/N mole ratio was used. At first, films of variable thickness were cast from this solution by Gardner's knife. However, the dry films were too fragile and mechanically not sufficient resistant to be handled. For this reason, composite specimens were obtained by coating commercial felts or nets with the $PDPrP{\cdot}nH^+$ solution. At the beginning, Cerablanket fabricated from synthetic aluminium silicate by Manville was used, nevertheless its dimensional stability was not satisfactory in humid environment. Successively, felts with 0.18 cm thickness (Sulfar S) and nets with 0.05 cm thickness and ca. 70% open area (Sulfar 1255) of poly-paraphenylensulfide (Ryton®) purchased from Testori, Novate Milanese (MI), were adopted.

The preparation of the composite materials was achieved by cycles consisting in the deposition of the PDPrP solution over each face of the felt or net and in the evaporation of the solvent, at 40°C. This procedure was continued until the final material thickness was 0.2 cm. The residual solvent was finally removed under vacuum. Gold layers electrodes (60 nm thick) were deposited by sputtering onto the two flat surfaces of the membrane.

2.3. Electrical conductivity measurements

The solid electrolyte was sandwiched between two steel discs having the same area (2.96 cm^2) of the gold films and connected to Pt wires. The whole assembly was then placed in a sealed-off glass cell specifically designed to be immersed in a thermostatic bath. The electrical conductivity was measured by the impedance spectroscopy technique using a 1255 Solartron Frequency Response Analyser. The measurements in dry conditions were performed after flowing nitrogen (N_2 grade 5 containing less than 3 ppm water supplied by Sapio, Milan) for four hours, in the presence of a silica gel layer on the bottom of the conductivity cell. The measurements at 11 and 33% RH were performed by placing in the cell chamber saturated aqueous solutions of LiCl or $MgCl_2$ respectively Accuracy of the above RH values in the experimental temperature ranges (Table I) was ±2% [18].

2.4. Other instrumental analyses

The solution NMR spectra were recorded on 200 AC Bruker Spectrometer. Chemical shifts (δ, ppm) were measured from internal TMS for ^1H resonance and from external 85% H_3PO_4 for ^{31}P resonance. ^{31}P CPMAS and MAS NMR spectra were run on a 300 Bruker instrument. MAS experiments were performed at a 90° pulse of 3 μs. A 30 s recycle delay was applied. CPMAS experiments were performed with contact times of 2–8 ms. DSC and TG analyses were carried out with a Mettler TA 3000 DSC instrument coupled to a Mettler TC10A TA microprocessor. Scans were performed at 10°C/min under N_2 flow unless otherwise indicated. X-ray powder diffraction (XRD) pattern were recorded with a computer controlled Phillips PW 1100 Diffractometer using the Ni filtered Cu K_α radiation. FT-IR spectra were recorded with a Nicolett FTIR Magna 560 instrument.

TABLE I Conductivity (σ, S cm^{-1}) of $PDPrP{\cdot}nH^+$ at $1H_3PO_4$/N mole ratio in PPS felt composite at variable temperature (T, K) and relative humidity (RH, %)

1st cycle (dry)		2nd cycle (11% RH)	
T	σ	T	σ
316	1.37×10^{-7}	313	1.55×10^{-7}
321	2.32×10^{-7}	315	1.97×10^{-7}
323	3.78×10^{-7}	319	3.25×10^{-7}
326	6.70×10^{-7}	322	6.26×10^{-7}
333	1.27×10^{-6}	323	8.24×10^{-7}
336	2.40×10^{-6}	327	1.36×10^{-6}
342	4.83×10^{-6}		
344	7.44×10^{-6}		
352	1.89×10^{-5}		

3. Results and discussion

3.1. Polymers characterization

PDPrP is soluble neither in any common solvent nor in 20% aqueous acetic acid. Therefore, contrary to the case of polydiethylphosphazene (PDET) [16], molecular weight data for PDPrP could not be determined by GPC. However PDPrP is soluble in pure acetic or formic acids allowing the polymer characterization by solution NMR spectroscopy; data were in agreement with the previous work [17]. The ^{31}P NMR spectrum of PDPrP in CD_3COOD solution (Fig. 1a) exhibits a main signal at about 27 ppm assigned to P in the polymer chain, and lower intensity signals due to P in terminal units. The relative area ratios of these signals allow to estimate molecular weight values of the order of 3×10^4 Da. The ^{31}P spectrum of solid PDPrP (Fig. 2a) shows a main signal at 21.1 ppm and a small signal at 13.1 ppm. Two couples of side bands are also visible. MAS and CP-MAS spectra recorded at variable contact time allowed to assign the main signal at 21.1 ppm to the chain P of the polymer crystalline phase, and the small signal at 13.1 ppm to P of the amorphous polymer phase. The XRD spectrum in Fig. 3 confirms the high cristallinity of the polymer. It should be pointed out that previous work for this polymer [17] evidenced the presence of two phases, an ordered crystalline phase and a thermotropic mesophase. The latter phase was characterized by less ordered molecular structure and by substantial mobility of the polymer side chains.

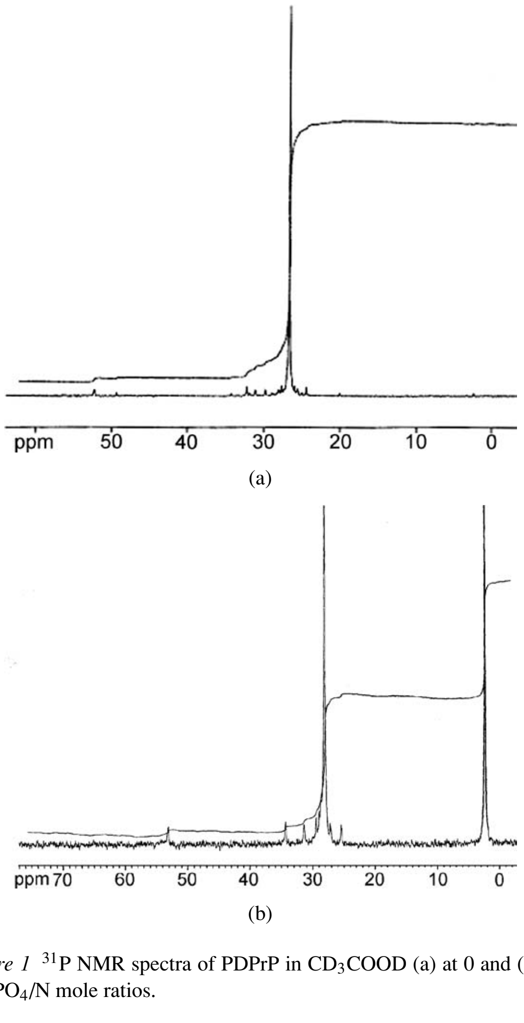

Figure 1 ^{31}P NMR spectra of PDPrP in CD_3COOD (a) at 0 and (b) at $1H_3PO_4/N$ mole ratios.

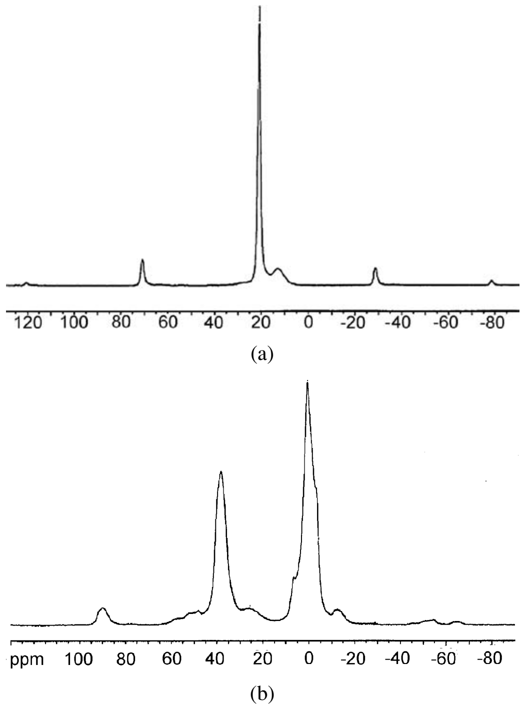

Figure 2 Solid state ^{31}P NMR spectra of freshly prepared PDPrP (a) at 0 and (b) $1H_3PO_4/N$ mole ratios.

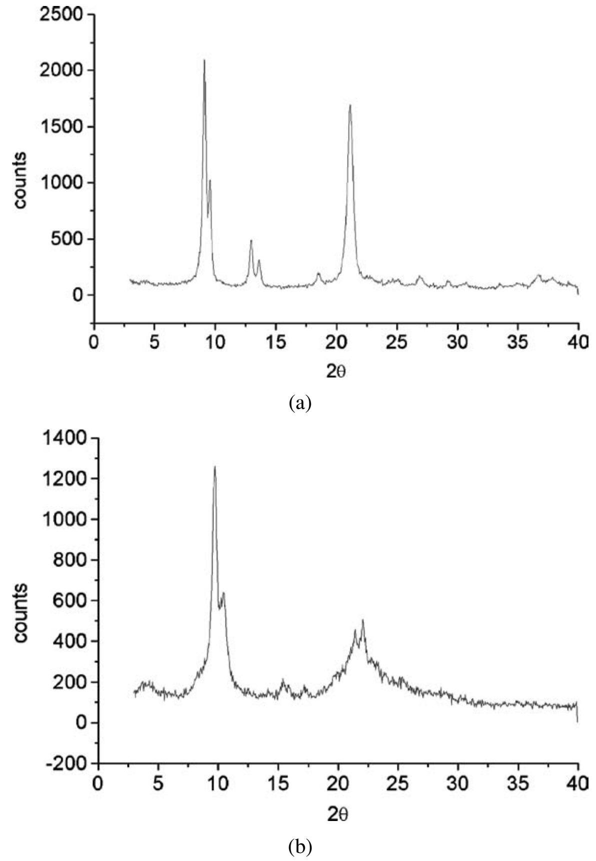

Figure 3 X-ray diffraction powder patterns of PDPrP (a) at 0 and (b) $1H_3PO_4/N$ mole ratios.

Finally, the thermal analysis for PDPrP in air indicated no weight loss to occur up to 333°C. It was evidenced by DSC scans the occurrence of a mesophase transition at 244°C, of melting at 300°C, and the absence of glass transition due to the high crystallinity degree (85%).

Similarly to PDPrP, PDPrP·nH$^+$ is soluble in pure acetic and formic acids, but not in water or diluted acid solution. The protonated polymer was characterised in the same way as the parent polymer. The solution ^{31}P NMR spectra of several PDPrP·nH$^+$ preparations up to $3H_3PO_4/N$ mole ratio exhibited the main signal due to P in the polymer chain at chemical shift varying from 27 (neat PDPR) to 32 (PDPrP·nH$^+$at $3H_3PO_4/N$ mole ratio) ppm. Other minor signals were also present in the spectra of the protonated polymer, as already observed for pure PDPrP. These signals were therefore assigned to P in terminal P=N units which were evident for the protonated polymer too. Their relative areas were roughly constant over the whole H_3PO_4/N mole ratio range, indicating that protonation did not alter significantly the parent polymer molecular weight distribution. In the spectra of the polymer containing H_3PO_4, the signal due to the protonating acid fell at 2.54–2.84 ppm. The area ratios of the protonating agent to the polymer ^{31}P resonance signals were in good agreement with the H_3PO_4/N mole ratio. A typical solution spectrum is shown in Fig. 1b for PDPrP·nH$^+$ at $1H_3PO_4/N$ mole ratio next to the spectrum of PDPrP.

The solid state spectrum of PDPrP·nH$^+$ (Fig. 2b) exhibits the signal due to the protonating agent at 0.88 ppm. The two other signals, at 38.5 and 25.6 ppm, arise from P in the protonated polymer chain. As already observed for PDPrP, these two signals are associated with the crystalline and amorphous phase, although in Fig. 2b they appear shifted downfield compared to Fig. 2a. The change of the chemical shifts ($\Delta\delta$ of the ^{31}P resonance signals upon protonation at nearly equimolar H_3PO_4/N ratio was much more marked in the solid state ($\Delta\delta = 17.3$ ppm) than in solution ($\Delta\delta = 1.51$ ppm). The chemical shift change observed in the solid state spectra confirms that N protonation by H_3PO_4 effectively occurs. N protonation was supported also from IR spectra. These showed a change of the most intense P=N stretching frequency from 1170 cm^{-1} for PDPrP to shorter wavelengths for PDPrP·nH$^+$. The frequency shift is in agreement with the expectation that N protonation induces a decrease of bond order by polarization. The spectra of the protonated polymer exhibited also two broad absorptions centred at 2400 cm^{-1} and at 2640 cm^{-1} due to OH stretching vibration in relatively short O···H···O bonded bridges, typical for most proton conducting materials [19, 20].

Other differences between PDPrP·nH$^+$ and PDPrP were shown by XRD spectroscopy and thermal analysis. The X-ray diffraction powder pattern of PDPrP·nH$^+$compared to PDPrP (Fig. 3) shows that the protonated polymer is definitely less crystalline than the parent polymer, but still maintains a significant degree of crystallinity. The TGA scans in air showed a marked decrease of the polymer degradation onset temperature upon protonation, i.e., from 333°C for PDPrP to 291°C for the polymer protonated (PDPrP·nH$^+$) at $3H_3PO_4/N$ mole ratio. The DSC scans for PDPrP·nH$^+$ showed a broad endothermic peak at 120–140°C upon heating from −100 to 200°C. However, in the second heating cycle, this endothermic peak was absent, and the glass transition at 10°C was evident.

3.2. Electrical characterization of composite membranes

Electrical conductivity measurements were carried out increasing the temperature from 29 to 79°C and in 0–33% relative humidity (RH) range. Under these conditions, the pure silicate and poly-paraphenylensulfide, PPS, materials show very high resistance ($>10^6\Omega$). The silicate felt was found to lose dimensional stability in humid environment, and therefore the data of the composite material with PDPrP·nH$^+$ are not reported here. PPS was available in form of a densely knitted felt of 0.10 cm thickness and a rather loosely assembled net having 0.05 cm thickness and 70% open area. After the polymer deposition, the membranes had almost equal thickness: 0.22 and 0.20 cm, respectively. The entrapped polymer amounts were 0.24 g/cm^2 for the net and 0.16 g/cm^2 for the felt. In Fig. 4a typical impedance spectrum of the felt is reported; as expected, a large increase in conductivity (i.e., a reduction of the circle diameter) is observed when the relative humidity rises. In all cases, the electrical conductivity (σ) was found to increase with T and RH (Tables I and II and Figs 5 and 6). At the first cycle the felt and the net showed approximately the same conductivity even if the amount of entrapped polymer was different. However the net (Figs 6 and 7 and Table II) showed a significant increase of conductivity from the first to the second dry cycle, and the values achieved in the second cycle kept constant in all subsequent dry cycles. The conductivity increase from the first to the second cycle may be due to thermal settlement of the material. The conductivity difference between the net at the second cycle (Table II) and the felt in the dry state (Table I) reflects the higher amount of PDPrP·nH$^+$ in the net. After several runs both at dry and at different RH conditions, upon returning to a dry cycle run, e.g., fifth up and down cycle, a slight increase of the conductivity was observed in comparison with the second cycle (Table II and Fig. 7).

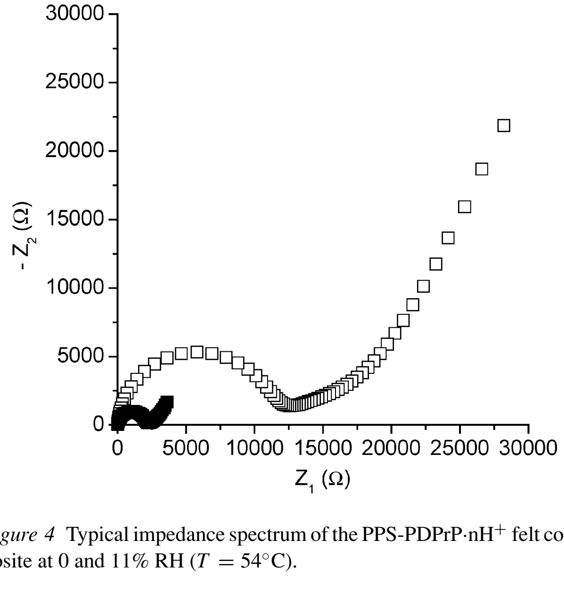

Figure 4 Typical impedance spectrum of the PPS-PDPrP·nH$^+$ felt composite at 0 and 11% RH ($T = 54$°C).

TABLE II Conductivity (σ, S cm^{-1}) of PDPrP·nH^{+} at 1H$_3$PO$_4$/N mole ratio in PPS net composite at variable temperature (T, K) and relative humidity (RH, %)

1st cycle (dry)		2nd cycle (dry)		3rd cycle (11% RH)		4th cycle (33% RH)		5th cycle up (dry)[a]		5th cycle down (dry)[a]	
T	σ	T	σ	T	σ	T	σ	T	σ	T	σ
303	1.44×10^{-7}	313	1.98×10^{-6}	304	7.46×10^{-7}	300	1.80×10^{-5}	302	8.67×10^{-7}	334	3.59×10^{-5}
307	2.36×10^{-7}	318	3.72×10^{-6}	308	1.39×10^{-6}	309	7.42×10^{-5}	304	1.25×10^{-6}	325	1.26×10^{-5}
314	4.24×10^{-7}	322	6.46×10^{-6}	311	2.57×10^{-6}	317	3.01×10^{-4}	309	2.22×10^{-6}	317	3.91×10^{-6}
323	1.34×10^{-6}	325	1.13×10^{-5}	313	4.70×10^{-6}	325	1.37×10^{-3}	314	4.31×10^{-6}	308	1.05×10^{-6}
331	4.16×10^{-6}	330	2.17×10^{-5}	317	8.66×10^{-6}			318	8.00×10^{-6}	301	2.36×10^{-7}
341	1.44×10^{-5}	334	4.44×10^{-5}	323	1.56×10^{-5}			322	1.40×10^{-5}		
		337	7.88×10^{-5}	326	3.03×10^{-5}			327	2.29×10^{-5}		
		342	1.38×10^{-4}	330	5.45×10^{-5}			331	3.37×10^{-5}		
				335	1.11×10^{-4}			339	7.08×10^{-5}		
				338	1.95×10^{-4}			342	1.04×10^{-4}		

[a] Values are listed in the measurement order, i.e., at the end the 4th cycle the system was flushed with N$_2$ while cooling to room temperature. The temperature was raised in the 5th cycle up to 68°C. The system was then cooled in the 5th cycle down until the temperature reached 28°C.

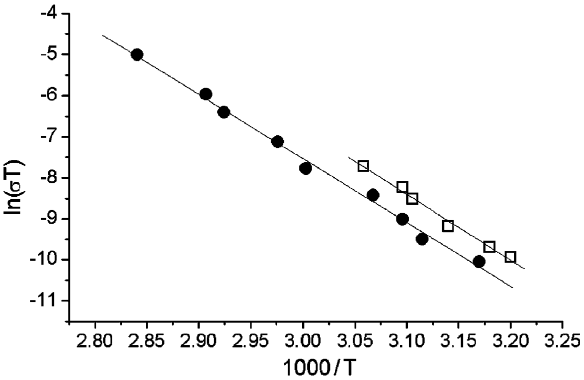

Figure 5 Plot of ln σT (S cm^{-1} K) vs. 1000/T (K^{-1}) for composite felt at 0% (●) and 11% RH (□).

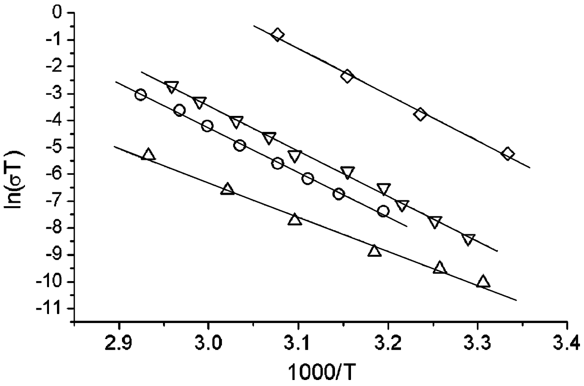

Figure 6 Plot of ln σT (S cm^{-1} K) vs. 1000/T (K^{-1}) for composite net at 0% RH in the 1st (△) and 2nd (○) heating cycles, and at 11% (▽) and 33% (◇) RH in the 3rd and 4th heating cycles, respectively.

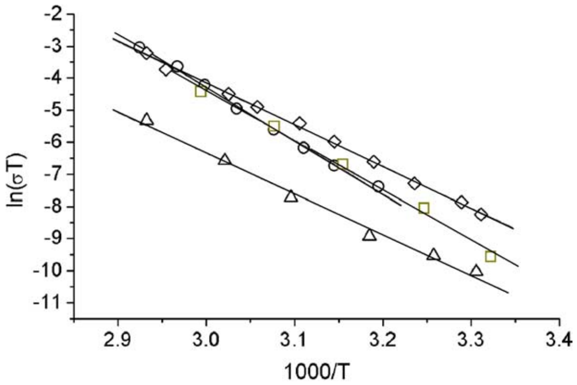

Figure 7 Plot of ln (σT, Ω^{-1} cm^{-1}K) versus 1/T (K^{-1}) for composite net at 0% RH in the 1st (△) and 2nd (○) heating cycles, and in the 5th cycle up (□) and 5th cycle down (◇).

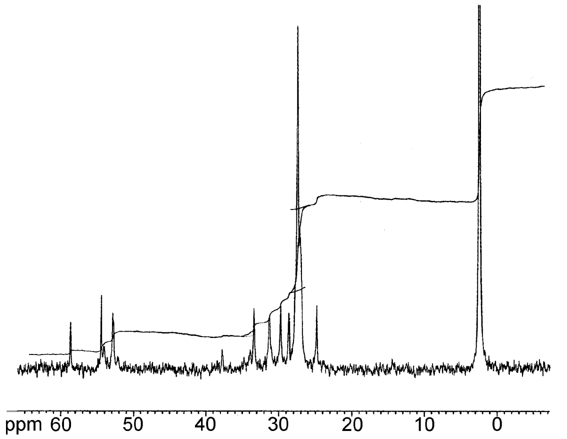

Figure 8 ^{31}P NMR spectrum of PDPrP·nH^{+} in CD$_3$COOD at 1H$_3$PO$_4$/N mole ratio extracted from the composite PPS net electrolyte at the end of the conductivity measurements.

For each run activation energies (Table III) were also calculated by least square fitting of ln σT vs. 1/T data (Figs 5–7). These data seem to point out that no major changes in the activation energy for the proton conduction process occur either because of the change of RH or because of the change of the type of composite material (i.e., the felt versus the net). Therefore, the conduction mechanism in these materials appears uninfluenced by the water vapour presence.

To find a cause for the conductivity increase after several runs and to verify possible polymer structure changes, a sample of the net composite after the 5th run was taken up in CD$_3$COOD (to extract the protonated phosphazene) and then the ^{31}P NMR spectrum was recorded (Fig. 8). The results show that, by comparison with the spectrum of freshly prepared PDPrP·nH^{+} at the same 1H$_3$PO$_4$/N mole ratio (Fig. 1b), the spectrum of the aged polymer in Fig. 8 exhibits a significant relative increase of the minor signals which had been assigned to the polymer terminal P=N units. This increase suggests a change in the chemical structure of

TABLE III Parameters of the linear regression of ln (σT, S cm^{-1} K vs. 1000/T (K^{-1}), according to the Arrhenius equation[a]: $\ln(\sigma T) = \ln\sigma_0 - (E/R) \times 1000/T$, for the 8 series of electrical measurements performed on the PDPrP·nH$^+$at 1H$_3$PO$_4$/N mole ratio in PPS felt and net composites at variable temperature (T, K) and relative humidity (RH, %)

	Felt		Net					
Parameters	1st cycle (dry)	2nd cycle (11% RH)	1st cycle (dry)	2nd cycle (dry)	3rd cycle (11% RH)	4th cycle (33% RH)	5th cycle up[b] (dry)	5th cycle down (dry)
E/R	15.61	16.07	12.70	16.57	16.78	17.17	12.94	15.47
$s(E/R)$	0.43	0.79	0.62	0.37	0.38	0.79	0.22	0.66
$\ln\sigma_0$	39.31	41.44	31.78	45.4	46.9	51.9	34.66	42.04
s($\ln\sigma_0$)	1.30	2.46	1.95	1.13	1.19	2.52	0.67	2.10
ρ	0.997	0.995	0.995	0.998	0.998	0.998	0.999	0.997
N	9	6	6	8	10	4	10	5
E(eV)	1.34	1.38	1.09	1.43	1.45	1.48	1.11	1.33

[a] Conductivity (σ), temperature (T), pre-exponential factor (σ_0), activation energy (E), gas constant (R), standard deviation (s) for the regression parameters, correlation coefficient (ρ), and number of (σ, T) value couples (N).

[b] At the end the 4th cycle the system was flushed with N$_2$ while cooling to room temperature. The temperature was raised to 68°C in the 5th cycle up. The system was then cooled in the 5th cycle down until the temperature reached 28°C.

the parent polymer due to the polymer aging under the experimental conditions of the conductivity measurements.

The experimental data allow to asses that ionic conductivity in the composite polyphenylensulfide-protonated polydipropylphosphazene (PPS-PDPrP·nH$^+$) is due to the presence of PDPrP·nH$^+$. This material shows 1.37×10^{-3} S cm^{-1}conductivity at relatively low temperature (52°C) and RH values (33%). Such an electrical conductivity value lays in the range reported for other polymers containing sulphonic or phosphonic acid groups [1, 4, 5] which were tested under similar experimental conditions. However, unlike the compounds containing —SO$_3$H functional groups where the activation energy for the proton conduction process strongly depends on RH [21], PDPrP·nH$^+$ appears to be unaffected by this drawback. Furthermore under dry operating conditions, PPS-PDPrP·nH$^+$exhibits higher conductivity ($\sigma = 10^{-4}$ S cm^{-1} at 69°C) than the above sulphonated polymers ($\sigma = 10^{-6}$–10^{-5} S cm^{-1} at 100°C) [22]. In dry conditions, the conductivity of the PPS-PDPrP·nH$^+$(1H$_3$PO$_4$/N mole ratio) composite is higher than that of other polymers containing basic N (as polydiallyldimethylammonium dihydrogenphosphate at 2H$_3$PO$_4$/N mole ratio [22] and poly(4-vinyl) imidazolium dihydrogenphosphate at 1H$_3$PO$_4$ mole per polymer repeating unit [7]) and comparable with the ethylene oxide oligomers terminated by imidazole groups ($\sigma = 10^{-4}$ S cm^{-1}) [23] or polybenzimidazole at 3H$_3$PO$_4$/N mole ratio [8].

4. Conclusions

By comparison with other major research polymers reported in literature, protonated polydipropylphosphazene (PDPrP·nH$^+$) appears a good candidate to develop solid proton conductors working at low RH. Although the conductivity properties of PDPrP·nH$^+$ are rather intriguing, solid electrolytes made entirely by this polymer cannot be fabricated due to its poor mechanical properties. However, the data obtained for the polyphenylensulfide-PDPrP·nH$^+$ composite indicate that fabrication of a composite material containing a polymer with good mechanical properties and PDPrP·nH$^+$ may allow to optimise both the mechanical and the conductivity properties of the electrolyte. As the NMR and conductivity data have shown that aging the polymer under the working experimental conditions of fuel cells yields structural changes of the polymer and apparent improvement of its conductivity, this aspect needs further investigation before optimisation of a composite solid electrolyte.

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