Final Draft
of the original manuscript:

Gomes, D.; Pereira Nunes, S.:
Fluorinated polyoxadiazole for high-temperature polymer electrolyte membrane fuel cells
In: Journal of Membrane Science (2007) Elsevier

DOI: 10.1016/j.memsci.2007.11.041

Fluorinated Polyoxadiazole for High Temperature Polymer Electrolyte Membrane Fuel Cells

*Dominique Gomes and Suzana P. Nunes**

GKSS Research Centre Geesthacht GmbH, Institute of Polymer Research,

Max Planck Str. 1, D-21502, Geesthacht, Germany

* Corresponding author. Tel.: +49 04152 87 2440; fax: +49 04152 87 2466

E–mail address: nunes@gkss.de (S.P. Nunes)

ABSTRACT: For the first time a fluorinated polyoxadiazole doped with phosphoric acid as a proton-conducting membrane for operation at temperatures above 100 °C and low humidities for fuel cells has been reported. Fluorinated polyoxadiazole with remarkable chemical stability was synthesized. No changes in the molecular weight (about 200,000 g mol^{-1}) can be observed when the polymer is exposed for 19 days to mixtures of sulphuric acid and oleum. Protonated membranes with low doping level (0.34 mol of phosphoric acid per polyoxadiazole unit, 11.6 wt.% H_3PO_4) had proton conductivity at 120°C and RH=100% in the order of magnitude of 10^{-2} S cm^{-1}. When experiments are conducted at lower external humidity, proton conductivity values drop an order of magnitude. However still a high value of proton conductivity (6 x 10^{-3} S cm^{-1}) was obtained at 150°C and with relative humidity of 1%. In an effort to increase polymer doping, nanocomposite with sulfonated silica containing oligomeric fluorinated-based oxadiazole segments has also been prepared. With the addition of functionalized silica not only doping level but also water uptake increased. For the nanocomposite membranes prepared with the functionalized silica higher proton conductivity in all range of temperature up to 120°C and RH=100% (in the order of magnitude of 10^{-3} S cm^{-1}) was observed when compared to the plain membrane (in the order of magnitude of 10^{-5} S cm^{-1}).

Keywords: polyoxadiazole, PEMFC, sulfonated silica, nanocomposite, proton conductivity, fuel cell

1. Introduction

Polymer electrolyte fuel cells are under extensive investigation as potential power source for mobile and stationary applications. One of the important challenges for the establishment of fuel cell as a competitive technology for energy conversion in the automotive sector is the development of alternative membranes with better performance than the current state-of-the-art perfluorinated ionomers such as Nafion® at temperatures higher than 100 °C and under external low humidification. The motivations for operating at high temperatures include improved reaction kinetics, minimization of catalyst poisoning by CO, simplification of the heat and water (humidification) management in the cell, improved gas transport and other issues associated with catalyst and design [1-3].

Among the high temperature polymer electrolyte membranes that have been developed so far, phosphoric acid doped polybenzimidazole [4,5] is certainly the most investigated system with high proton conductivity even at temperatures as high as 200 °C [5,6] and chemical and thermal stability. Despite of that, for further large scale applications of this polymer, new methods of syntheses should be explored to further increase mechanical properties, protonation level and/or functionalization of the polymer and processability.

Recently, we have indeed tested proton conductive membranes based on dense sulfonated and/or protonated diphenyl ether polyoxazole membranes exhibiting high proton conductivity values (order of magnitude of 10^{-1} -10^{-2} S cm^{-1} at 50-80°C) [7,8] and with highly oxidative stability in Fentons's reagent retaining 98-100% of their weight. However, due to the ether electron-donor substituent (-O-) in *para* position to the aromatic sulfonic acid groups, which decreases the polymer hydrolytic stability in humidified environments at temperatures higher than 100 °C [9], these polyoxazoles became brittle when operating at temperatures higher than 80°C. In the present work, we changed the ether electron-donor substituent by an electron-withdrawing group (-C-$(CF_3)_2$-) in *para* position to the aromatic groups which should increase both stability and acidity of the polyoxadiazole already containing a strong electron-withdrawing ring. So far, fluorinated polyoxadiazoles, a polymer with a heterocyclic ring and also with very high chemical and thermal stabilities have not been used for fuel cells at temperatures higher than 100 °C and low humidities.

An advantage of polyoxadiazoles in comparison to the polybenzimidazoles in the lower reaction temperature and time required for the synthesis (up to 5h at 160°C) in contrast to the polybenzimidazoles (up to 24h at 200°C). An additional point is the better film forming capability of the polyoxadiazoles synthesized in this paper, which can be dissolved at room

temperatures in organic solvents while for most polybenzimidazoles the dissolution in organic solvents occurs at high tempeatures (higher than 200°C) in pressurized reactors [4,6].

Here, we report for the first time, the use of a fluorinated polyoxadiazole doped with phosphoric acid as a proton-conducting membrane for operation at temperatures above 100 °C and low humidities for fuel cells. In an effort to increase even more proton conductivity, nanocomposite with sulfonated silica containing fluorinated-based oxadiazole telechelic has also been prepared. The synthesis and characterization of the functionalized silica with thermal stability up to 160 °C have been reported by us elsewhere [10]. The polymer is very stable even in mixtures of sulfuric acid and oleum (20-65 % SO_3). After several days practically no changes of molecular weight were detected.

2. Experimental Section

2.1. Materials

4,4'-dicarboxyphenyl-hexafluorpropane, HF (99%, Aldrich), fuming sulfuric acid, oleum (puriss. pa. 20% SO_3, Riedel-de Häen and 65%, Merck), hydrazine sulfate, HS (>99%, Aldrich), N-methyl-2-pyrrolidone, NMP (99%, Aldrich), sodium hydroxide, NaOH (99%, Vetec), sulfuric acid (95-97%, Vetec), phosphoric acid (85%, Aldrich), poly(phosphoric acid), PPA (Aldrich). All chemicals were used as received. Functionalized silica was synthesized and characterized as described elsewhere [10] and depicted in Scheme 1.

2.2. Poly(hexafluor propane-1,3,4-oxadiazole) synthesis

Poly(hexafluor propane-1,3,4-oxadiazole) was synthesized using conditions analogous to those previously optimized for diphenyl ether polyoxadiazoles [11,12]. After reacting 4,4'-dicarboxyphenyl-hexafluorpropane and hydrazine sulfate for 3h at 160 °C, the reaction medium was poured into water containing 5% w/v of sodium hydroxide, for precipitation of the polymer. The pH of this polymer suspension was controlled according to literature [11]. The chemical structure of polymer is depicted in Figure 1. Yield = 89%. ^{1}H-NMR ($CDCl_3$): δ = 8.21-8.18 (4 H_1, d), 7.62-7.60 (4 H_2, d) (Figure 1).

($C_{17}H_8N_2O_1F_6$) (370): Calcd. % C 55.1, H 2.2, N 7.6; Found C 55.3, H 3.2, N 6.6.

2.3. Polymer sulfonation

Attempts to sulfonate the polymer were based on post-sulfonation routes by reacting the polymer with sulfuric acid (95-97%) and fuming sulfuric acid (20-65% SO_3) at 45°C from 1

to 19 days. As a typical example, 1g of fluorinated polyoxadiazole polymer was dissolved in 15 mL of a mixture containing 10 ml of concentrated sulfuric acid (95-97%) and 5 ml of oleum with 20% SO_3 (2:1) and vigorously stirred at 45°C. Then, the polymer solution was gradually precipitated into ice-cold water containing K_2CO_3 under mechanical stirring until achieving a neutral pH. The polymer precipitate was filtered, washed several times with distilled water and dried for 12h at 80 °C.

2.4. Structural Characterization

The polymer structure was characterized by elemental analysis, ^{1}H-NMR and infrared spectroscopy. Elemental analysis was conducted on a Carlo Erba Elemental Analyzer-Mod 1108. ^{1}H-NMR spectra were obtained in $CDCl_3$ at 25°C using a Bruker DMX-300 spectrometer. Infrared spectra were recorded on a Bruker Equinox IFS 55 spectrophotometer in the range 4000-400 cm^{-1}, using polymer films.

2.5. Molecular weight measurements

A Viscotek SEC apparatus equipped with Eurogel columns SEC 10.000 and PSS Gram 100, 1000, with serial numbers HC286 and 1515161 and size 8 x 300 mm was employed to evaluate the weight average molecular weights of polymer samples. The equipment was calibrated using polystyrene standards (Merck) with weight average molecular weights ranging from 309 to 944,000 g/mol. A solution with 0.05 M lithium bromide in DMAc was used as the carrier.

2.6. Membrane preparation and characterization

Homogeneous membranes were cast from solutions with a polymer concentration of 4 wt. % in NMP. After casting, the NMP was evaporated in a vacuum oven at 60°C for 24h. For further residual solvent removal, the membranes were immersed in water bath at 60°C for 48h and dried in a vacuum oven at 60°C for 24h. The final thickness of the membranes was about 60 μm.

Nanocomposite membranes were prepared by adding 5 wt.% of functionalized silica (based on polymer content) into the 4 wt.% polymeric solution. The solution was stirred for 6h and cast on a glass plate at 60°C for solvent evaporation and dried following the same protocol described for the membranes prepared only with the polymer. The final thickness of the membranes was about 70 μm.

Protonated membranes were prepared by immersing dried membrane samples into 85 % phosphoric acid solution at 25 °C for 7 days.

The membrane morphology was observed by scanning electron microscopy (SEM) type LEO 1550VP. The samples were previously coated with gold in a sputtering device.

2.7. Water and phosphoric acid uptake

Water and phosphoric acid uptake was measured by immersing two samples (around 100 mg each) of membrane in deionized water and phosphoric acid (85%) bath conditioned at 25°C for 24h and 7 days, respectively. Before measuring the weights of the hydrated membranes, the water or phosphoric acid was removed from the membrane surface by blotting with a paper towel. The water or phosphoric acid uptake was calculated as the ratio (in weight) of adsorbed water or phosphoric acid on the dry sample weight. The water or phosphoric acid uptake values reported correspond to the average value of the two samples.

2.8. Thermal and mechanical analysis

Thermogravimetric analysis (TGA) experiment was carried out in a Netzsch 209 TG, equipped with a TASC 414/3 thermal analysis controller. The polymer sample, under nitrogen atmosphere, was heated from 100 to 700°C at 10°C/min. The second heating was used for polymer characterization.

Differential scanning calorimetry (DSC) measurements were performed in a Netzsch 204 DSC, equipped with a TASC 414/2 thermal analysis controller. Polymer film sample was placed in aluminum sample pan, and the temperature was increased with a heating rate of 20°C/min from 100 to 450°C, under nitrogen atmosphere.

Dynamic mechanical thermal analysis (DMTA) was used for determination of glass transition temperature (T_g), storage modulus (E'), loss modulus (E'') and loss tangent (Tan δ). DMTA was performed using a TA instrument RSA 2 with a film tension mode at a frequency of 1Hz and 0.1 N initial static force. The temperature was varied from 25 to 400 °C at a heating rate of 2°C/min and at a constant strain of 0.05%.

2.9. Proton Conductivity

Proton conductivity was measured by the AC impedance spectroscopy in the frequency range 10-10^6 Hz at signal amplitude ≤ 100 mV and obtained from the impedance modulus at zero phase shift (high frequency side) with 20 to 100% of relative humidity (RH). Measurements were performed with a flow cell purged with wet nitrogen; the relative humidity was controlled by bubbling nitrogen gas in water heated at a suitable temperature. The impedance measurements were carried out on stacks containing up to five membranes

(cumulative thickness around 500 μm). The spectrometer used was a Zahner IM6 electrochemical workstation.

3. Results and Discussion

3.1. Chemical Stability of the Poly(hexafluor propane-1,3,4-oxadiazole)

Attempts to sulfonate the poly(hexafluor propane-1,3,4-oxadiazole) performed in mixtures of concentrated sulfuric acid (95-97 %) and oleum (20-65% SO_3) confirm the high chemical stability of this polymer. Two different concentration of oleum were used 20 and 65%, respectively. Table 1 shows the polymer characterization results as a function of post-sulfonaton time, including elemental analysis results (S/C and N/C), the average mass molecular weights (Mw) and the polydispersity (D) determined by size exclusion chromatography (SEC). In Figure 2 the SEC profiles relative to polystyrene standard for the samples treated at different conditions are shown. The analysis of the results shown in Table 1 indicates that the attempts to sulfonate the polymer were not successful. Figure 2 confirms the very high chemical stability of the polymer. Indeed after treatment with mixture of concentrated sulfuric acid and oleum with 20% SO_3 for 19 days no changes in the average molecular weights were observed, indicating that the polymer does not degradate after treatment. After 6 days in the mixture of sulfuric acid and oleum with 65% SO_3, the molecular weight slightly decreased while the polymer became less polydisperse (Figure 2.b). For the samples treated with mixtures of sulfuric acid and oleum with 65% SO_3, this decrease of polydispersity may be attributed to the disruption of the three-dimensional crosslinked linkages [12] eventually present in polymer samples with molecular weight in the order of magnitude of 10^6 g mol^{-1} as well as the solubilization of species with lower molecular weights in the order of magnitude of 10^4 g mol^{-1}.

The electron withdrawing effect of both groups, fluorine and oxadiazole, which deactivates the benzene ring, hinders the sulfonation reaction by an electrophilic substitution route. That is the reason why no sulfonation took place and all samples have a negligible S/C rate. The analysis of the elemental results also indicates that after treatment in acid the experimental N/C ratio increases reaching values more closed to the theoretical one (N/C = 0.138), expected for the structure depicted in Figure 1, indicating that the polymerization was further continued during the acid treatment. Though experimental N/C values are slightly lower than the theoretical one, no residual hydrazide groups are present in the polymer. The ^{1}H-NMR spectrum of the poly(hexafluor propane-1,3,4-oxadiazole) without hydrogen

resonances in the range 9-10 ppm (Figure 1) confirms the absence of residual hydrazide NH groups [13] as well as by the analysis of the TGA spectrum (shown in Figure 3 and discussed in section 3.2.).

The replacement of the ether electron-donor substituent (-O-) in *para* position to the aromatic sulfonic acid groups by an electron-withdrawing group (-C-$(CF_3)_2$-) in *para* position increased significantly the chemical stability of the polyoxadiazole. While for polyoxadiazole containing diphenyl ether groups after treatement for 1 h in lower acid concentration, 3:1 volume ratio of H_2SO_4: oleum (20% SO_3), the molecular weight decreased significantly (from 358000 to 17000 g mol^{-1}) [14], for the fluorinated polyoxadiazole no changes in the molecular weight could be observed even in more drastic conditions, 19 days in 2:1 volume ratio H_2SO_4: oleum (20% SO_3).

3.2. Thermal and mechanical analysis of the poly(hexafluor propane-1,3,4-oxadiazole)

The thermal stability of the poly(hexafluor propane-1,3,4-oxadiazole) was analyzed by thermogravimetric analysis (TGA) and dynamic mechanical thermal analysis (DMTA), as shown in Figures 3 and 4. No weight losses of eventually absorbed water were detected in the temperature range from 20 to 150 °C. Furthermore in the range of temperatures between 275 and 375 °C no loss of water which could result from conversion of hydrazide groups to oxadiazole [13] was observed. These results confirm the high hydrophobicity of the polymer starting first at 430°C confirms its high thermal stability (Figure 3).

The mechanical property of the polymer was evaluated by means of DMTA. Good dimensional stability and high storage modulus (E') of about 1 GPa at 250°C (Figure 4) were observed.

3.3. Water uptake, doping level and T_g of fluorinated polyoxadiazole membranes

When polymers with basic nitrogens are doped by immersing them in acid baths, the acid is absorbed and equilibrium is achieved after a certain time. Recently, we have shown that complete protonation of sulfonated polyoxadiazole containing diphenyl ether group attached to the main by sulphuric acid can be achieved after 48h [8]. In the present work, membranes were soaked for 7 days in concentrated phosphoric acid to guarantee that equilibrium was achieved. Table 2 shows the doping level achieved by the membranes, which has been measured by means of H_3PO_4 uptake (wt.%) and reported in terms of the mol number of acid molecules per monomeric unit. In the literature, it has been reported for other polymers that the doping level can be varied by polymer immersion in acid baths with different

concentrations [5,6,8,15]. Taking into account the high hydrophobicity of the poly(hexafluor propane-1,3,4-oxadiazole) with very low water absorption capability (about 3 wt.%) when immersed in water at different temperatures (Table 2) or when exposed to humid atmosphere we opted to use a high phosphoric acid concentration bath (85 % ~ 15 M). As one may see in Table 2, very low doping level was achieved (0.34 mol of phosphoric acid per polyoxadiazole unit), corresponding to only one proton for three nitrogen atoms able to be protonated.

3.4. Nanocomposites with functionalized silica

In an effort to increase the polymer doping, nanocomposites containing silica modified with sulfonated oxadiazole telechelics have also been prepared. The synthesis and characterization of the functionalized silica have been reported by us elsewhere [10]. The analysis of Table 2 indicates that with the addition of functionalized silica not only the doping level but also the water uptake increased, as should be expected.

Due to the high polymer hydrophobicity, there is a clear segregation of the functionalized silica with formation of cavaties around the hydrophilic silica particles. As a result a sponge like structure with closed cells is formed (Figure 5), in contrast to the plain polymer membrane which is pore free. As a consequence two other thermal transitions additionally to the polymer's T_g at 304°C are observed. The additional transitions might be associated to the T_g of the low molecular weight (about 9000 g mol^{-1}) [16] sulfonated oxadiazole oligomeric segments attached to the silica surface. The lower Tg at 139°C might be attributed to the non-sulfonated segments, while the higher T_g at 180°C is related to the part of the chain, which is sulfonated. The introduction of bulky substituent on the aromatic rings as well as the increase of chain-chain interactions are the main reason for the increase of T_g with sulfonation [17].

On the other hand, when this functionalized silica was added to sulfonated polyetherketone (SPEEK) a porous free was obtained since the compatibility between the sulfonated oligomers and the polymer matrix was high [10].

3.5. Proton conductivity

Figure 6 shows the dependence of the proton conductivity on the temperature for the poly(hexafluor propane-1,3,4-oxadiazole) membranes at relative humidity equal to 100 % is shown. As expected, the proton conductivity of the non protonated plain polymer is very low (in the order of magnitude of 10^{-5} S cm^{-1}).

Much higher proton conductivity values were obtained for the protonated membranes with phosphoric acid (in the order of magnitude of 10^{-2} S cm^{-1}). Taking into account the low

doping level of the polymer (0.34 mol of phosphoric acid per polyoxadiazole unit, 11.6 wt.% H_3PO_4), the proton conductivities may be considered high. For instance, polybenzimidazole with a doping level equal to 3 (40 wt.% H_3PO_4), which is 10-fold higher then that for the protonated polyoxadiazole in this paper, has a proton conductivity in the order of magnitude of 10^{-3} S cm^{-1} at room temperature [18]. In phosphoric acid doped polyoxadiazole membranes, as well as in the case of polybenzimidazoles, hydrogen bonds can be established between the nitrogens of the polymer and the water and acid molecules favoring the proton transport. In the case of the polymer reported here an additional factor seems to play an important role. The electronegative fluor atoms probably have significant contribution to the formation of hydrogen bonds with the phosphoric acid. Figure 7 shows the proposed interactions between the polymer and H_3PO_4.

For the nanocomposite membranes prepared with the functionalized silica higher proton conductivity compared to the plain membrane was observed in all range of temperature (in the order of magnitude of 10^{-3} S cm^{-1}). Similar results have been reported by us [10], when this functionalized silica was added to SPEEK and attributed to the amphoteric character of the sulfonated oxadiazole oligomeric segments containing both sulphonic acid groups and basic nitrogen sites (Scheme 1). Improved proton conductivities can be obtained due to the presence of pyridine-like nitrogen sites near sulfonic groups, which can be seen as additional points for proton jumps. An additional factor in the case of nanocomposites with the hydrophobic fluorinated polyoxadiazole is the higher water absorption by the functionalized silica, which assures a better water retention at high temperatures.

In Figure 6, experiments were performed with relative humidity (RH) equal to 100%. The presence of water promotes the dissociation of the acid, increasing the number of charge carriers and consequently the proton conductivity. When experiments are conducted at lower external humidity (Figure 8), the proton conductivity values drop at least an order of magnitude. With further increase of temperature, with simultaneous decrease of RH, an increase of proton conductivity was obtained. As discussed in details by He et al. [18] for polybenzimidazole, there is a significant conductivity dependence of acid doped basic polymers on the relative humidity (RH) at high temperatures. The higher the temperature, the more significant the RH effect, especially when the RH value is very low. Similar trends have also been reported in other published works [5,19].

Taking into account the low water uptake of the polymer and the porosity of the nanocomposite prepared with the functionalized silica without protonation, the pores creates an additional resistance and might explain the very low proton conductivity obtained at low

humidity conditions. The protonated nanocomposite containing functionalized silica have higher proton conductivity, reaching the value of 5.35 x 10^{-3} S cm^{-1} at 120°C and RH = 5%, which can be explained by the higher doping level (0.45 mol of phosphoric acid per polyoxadiazole unit, 15.6 wt.% H_3PO_4) achieved as well as higher water retention capacity at higher temperatures. The water absorption was particularly increased with the addition of functionalized silica, followed by protonation. The contribution of different factors to this observation can be better understood by analysing the FTIR spectra of the protonated and nanocomposite poly(hexafluor propane-1,3,4-oxadiazole) films (Figure 9). As one may see, the peaks related to the absorbed water at 3367 cm^{-1} and at 2911 cm^{-1} assigned to the O-H stretch of the hydrogen-bonded groups intramolecular and intermolecular, respectively, are observed for the protonated polymers and nanocomposites. This result supports once more the high hydrophobicity of the polymer, showing no water absorption when exposed to the atmospheric moisture. The protonation of the polymer nitrogens by the phosphoric acid and/or water resulting in hydrogen-bonded nitrogen (N^+-H) is observed at 2345 cm^{-1}. The intense peaks at 1005 cm^{-1} related to the siloxane stretching (ν Si-O-Si) and at 1003 cm^{-1} related to the phosphorous stretching (ν P-O) are observed for the nanocomposite and protonated films, respectively. The peak at 1621 cm^{-1} assigned to the angular vibration of water is much higher for the protonated polymer with functionalized silica. This peak is characteristic of the adsorbed water in inorganic particle surfaces or incorporated water into the crystal lattice [20,21]

The approaches described in literature to increase the doping level of basic polymers are the immersion in polyphosphoric acid baths with different concentrations [5,6], the sulfonation of the polymer and the direct casting of the polymeric solution from the reactor [4,5] immediately after synthesis. While the proton conductivity increases with the doping level of the polymer, the mechanical properties might be affected and a compromise between absorbed acid and mechanical properties has to be achieved in many situations. He et al. [19] reported that the mechanical properties of PBI significantly decreases with immersion in acid and acceptable mechanical properties are limited to a doping level of 3-8 mol of phosphoric acid per PBI unit [19]. However, recently Xiao et al. [4] have reported doped PBI with doping levels varying from 15 to 25 mol of phosphoric acid per PBI unit and still with good mechanical properties. The exploration of new structures as well as the increase of the molecular weight of this class of polymer may potentially impact the increase of proton conductivity as a consequence of the increase of polymer doping without significant detriment of mechanical properties of the polymer.

Based on the encouraging results shown in the present work regarding the high chemical stability with no changes in the molecular weight when the polymer is exposed for 19 days to mixtures of sulphuric acid and oleum, the high thermal stability (up to 430°C) and the high proton conductivity obtained (10^{-3} S cm^{-1} at 150°C and RH=1%) with very low doping level (0.34 of phosphoric acid per polymer unit), it can be affirmed that the use of this fluorinated polyoxadiazole doped with phosphoric acid as a proton-conducting membrane for operation at temperatures above 100 °C and low humidities for fuel cells may be promising. Now, attempts to increase the doping level by functionalization of the polymer using alternative routes such as nucleophilic aromatic substitution (metalation) [22] and functionalized monomers [16] are underway.

4. Conclusions

Fluorinated polyoxadiazole with high chemical and thermal stability with glass-transition temperatures (T_g) of 304°C and initial degradation temperature of 430°C, with good mechanical properties (storage modulus about 1 GPa at 250°C) has been prepared. No changes in the molecular weight (about 200000 g mol^{-1}) can be observed when the polymer is exposed for 19 days to mixtures of sulphuric acid and oleum.

Phosphoric acid doped membranes based on the fluorinated polymer containing or not sulfonated silica have been prepared and characterized. With the addition of functionalized silica not only the doping level but also the water uptake increased. For the nanocomposite membranes prepared with the functionalized silica higher proton conductivity in all range of temperatures up to 120°C and RH=100% (in the order of magnitude of 10^{-3} S cm^{-1}) was observed compared to the plain polymer (in the order of magnitude of 10^{-5} S cm^{-1}) and attributed to the amphoteric character of the sulfonated oxadiazole oligomeric segments attached to the silica containing both sulphonic acid groups and basic nitrogen sites as well as to the better water retention of the membrane due to the presence of silica.

Protonated membranes with low doping level (0.34 mol of phosphoric acid per polyoxadiazole unit, 11.6 wt.% H_3PO_4) have proton conductivity at 120°C and RH=100% in the order of magnitude of 10^{-2} S cm^{-1}. When experiments are conducted at lower external humidity, proton conductivity values drop an order of magnitude, but are still high compared to other polymers reported in the literature. Values of 6.11 x 10^{-3} S cm^{-1} at 150°C and with relative humidity of 1% have been obtained.

Acknowledgments. The work was part of the Helmholtz-Hochschul-Nachwuchsgruppe Projekt (VH-NG-323) and Virtual Institute on Asymmetric Structures for Polymer Electrolyte

Fuel Cell (VH-VI-139) sponsored by the Helmholtz Association. The authors thank S. Nowak for the TGA and DSC measurements, H. Böttcher for the dynamic mechanical thermal analyses, T. Emmler for the NMR spectrum and K. Prause for the SEM images.

References

[1] Q. Li, R. He, J.O. Jensen, d N.J. Bjerrum, Approaches and Recent Development of Polymer Electrolyte Membranes for Fuel Cells Operating above 100 °C, Chem. Mater., 15 (2003) 4896-4915.

[2] A. Faghri, Z. Guo, Challenges and opportunities of thermal management issues related to fuel cell technology and modeling, International Journal of Heat and Mass Transfer 48 (2005) 3891-3920.

[3] J. Zhang, Z. Xie, J. Zhang, Y. Tang, C. Songa, T. Navessin, Z. Shi, D. Songa, H. Wang, D.P. Wilkinson, Z.-S. Liu, S. Holdcroft, High temperature PEM fuel cells, Journal of Power Sources, 160 (2006) 872-891.

[4] L. Xiao, H. Zhang, T. Jana, E. Scanlon, R. Chen, E.-W. Choe, L.S. Ramanathan, S. Yu, B.C. Benicewicz, Synthesis and Characterization of Pyridine-based Polybenzimidazoles for High Temperature Polymer Electrolyte Membrane Fuel Cell Applications, Fuel Cells, 5 (2005) 287-295.

[5] J.A. Asensio, P. Gómez-Romero, Recent Developments on Proton Conducting Poly(2,5-benzimidazole) (ABPBI) membranes for high Temperatures Polymer Electrolyte Membrane Fuel Cells, Fuel Cells, 5 (2005) 336-343.

[6] J. Lobato, P. Canizares, M.A. Rodrigo, J.J. Linares, G. Manjavacas, Synthesis and characterisation of poly[2,2-(m-phenylene)-5,5-bibenzimidazole] as polymer electrolyte membrane for high temperature PEMFCs, Journal of Membrane Science, 280 (2006) 351-362.

[7] D. Gomes, J. Roeder, M.L. Ponce, S.P. Nunes, Characterization of partially sulfonated polyoxadiazoles and oxadiazole-triazole copolymers, Journal of Membrane Science, 295 (2007) 121-129.

[8] J. Roeder, D. Gomes, M.L. Ponce, V. Abetz, S.P. Nunes, Protonation of Sulfonated Poly(4,4-diphenylether-1,3,4-oxadiazole) Membranes, Macromolecular Chemistry and Physics 208 (2007) 467 -473.

[9] M. Schuster, K.-D. Kreuer, H.T. Andersen, J. Maier, Sulfonated poly(phenylene sulfone) polymers as hydrolytically and thermooxidatively stable proton conducting ionomers, Macromolecules, 40 (2007) 598-607.

[10] D. Gomes, I. Buder, S.P. Nunes, Sulfonated silica-based electrolyte nanocomposite membranes, Journal of Polymer Science Part B: Polymer Physics 44 (2006) 2278-2298.

[11] D. Gomes, C. Borges, J.C. Pinto, Effects of reaction variables on the reproducibility of the syntheses of poly-1,3,4-oxadiazole, Polymer, 45 (2004) 4997-5004.

[12] D. Gomes, C.P. Borges, J.C. Pinto, Study of the synthesis of poly(4,4'-diphenylether-1,3,4-oxadiazole) in solutions of poly(phosphoric acid), Polymer, 42 (2001) 851-865.

[13] D. Gomes, J.C. Pinto, C. Borges, Determination of hydrazide content in poly(oxadiazole-hydrazide) copolymers by NMR and thermal analysis, Polymer 44 (2003) 6223-6233.

[14] D. Gomes, J. Roeder, M.L. Ponce, S.P. Nunes, Single-Step Synthesis of Sulfonated Polyoxadiazoles and their use as Proton Conducting Membranes, submitted to Journal of Power Sources.

[15] R. Bouchet, E. Siebert, Proton conduction in acid doped polybenzimidazole, Solid State Ionics, 118 (1999) 287-299.

[16] D. Gomes, S.P. Nunes, Synthesis and Characterization of Poly(arylene ether oxadiazole) Telechelics, Macromolecular Chemistry and Physics 204 (2003) 2130-2141.

[17] A. Noshay, L.M. Robeson, Sulfonated Polysulfone, Journal of applied polymer science, 20 (1976) 1885-1903.

[18] R. He, Q. Li, G. Xiao, N.J. Bjerrum, Proton conductivity of phosphoric acid doped polybenzimidazole and its composites with inorganic proton conductors, Journal of Membrane Science, 226 (2003) 169-184.

[19] R. He, Q. Li, A. Bach, J.O. Jensen, N.J. Bjerrum, Physicochemical properties of phosphoric acid doped polybenzimidazole membranes for fuel cells, Journal of Membrane Science, 277 (2006) 38-45.

[20] G. Socrates, Infrared and Raman Characteristic Group Frequencies Tables and Charts John Wiley & Sons, Chichester, 2001.

[21] A.S. Arico, V. Baglio, A.D. Blasi, V. Antonucci, FTIR spectroscopic investigation of inorganic fillers for composite DMFC membranes, Electrochemistry Communications, 5 (2003) 862-866.

[22] J. Kerres, W. Cui, S. Reichle, New Sulfonated Engineering Polymers via the Metalation Route. 1. Sulfonated Poly(ethersu1fone) PSU UdeP via Metalation-Sulfination-Oxidation, Journal of Polymer Science: Part A Polymer Chemistry, 34 (1996) 2421-2438.

Table 1: Polymer characterization results as a function of post-sulfonaton time in mixtures of fuming sulfuric acid (20-65% SO_3) and sulfuric acid (95-97%) at 45°C.

Sample	Solvent [a] H_2SO_4- **x** % SO_3	time (day)	S/C	N/C	Mw (g mol^{-1})	D
1	-	-	0	0.119	198000	2.96
2	x = 20% SO_3	1	0	0.134	134000	1.88
3		5	0	0.134	148000	2.50
4		12	0	0.131	205000	3.28
5		19	0	0.132	210000	1.68
6	x= 65% SO_3	2	0	0.137	112000	1.27
7		6	0	0.130	97000	1.19

[a] 2:1 vol. ratio of H_2SO_4 :SO_3

(Table 1)

Table 2: Water uptake, doping level and T_g of fluorinated polyoxadiazole membranes

Membrane	IEC (mequiv g^{-1})	Doping Level [a]	H_3PO_4 uptake (wt.%)	Water uptake (wt. %)		T_g (°C)	
				25°C	60°C	DSC	Tan δ
plain polymer	0	0.34	11.6	2.8	2.5	295	304
polymer with functionalized silica	0.038	0.45	15.6	5.2	5.4	[b]	310 139, 180

[a] mol of phosphoric acid per fluorinated polyoxadiazole unit; [b] not measured.

(Table 2)

Figure captions

Scheme 1: Structure of the functionalized silica.

Figure 1: ^{1}H-NMR spectrum of the poly(hexafluor propane-1,3,4-oxadiazole) (spectrum taken in $CDCl_3$).

Figure 2: SEC profiles (relative to polystyrene standard) for polymer samples treated at different times with mixtures of sulfuric acid and oleum with 20% SO_3 (a) and 65% SO_3 (b), respectively.

Figure 3: TGA curve for the poly(hexafluor propane-1,3,4-oxadiazole).

Figure 4: DMTA plot of the poly(hexafluor propane-1,3,4-oxadiazole).

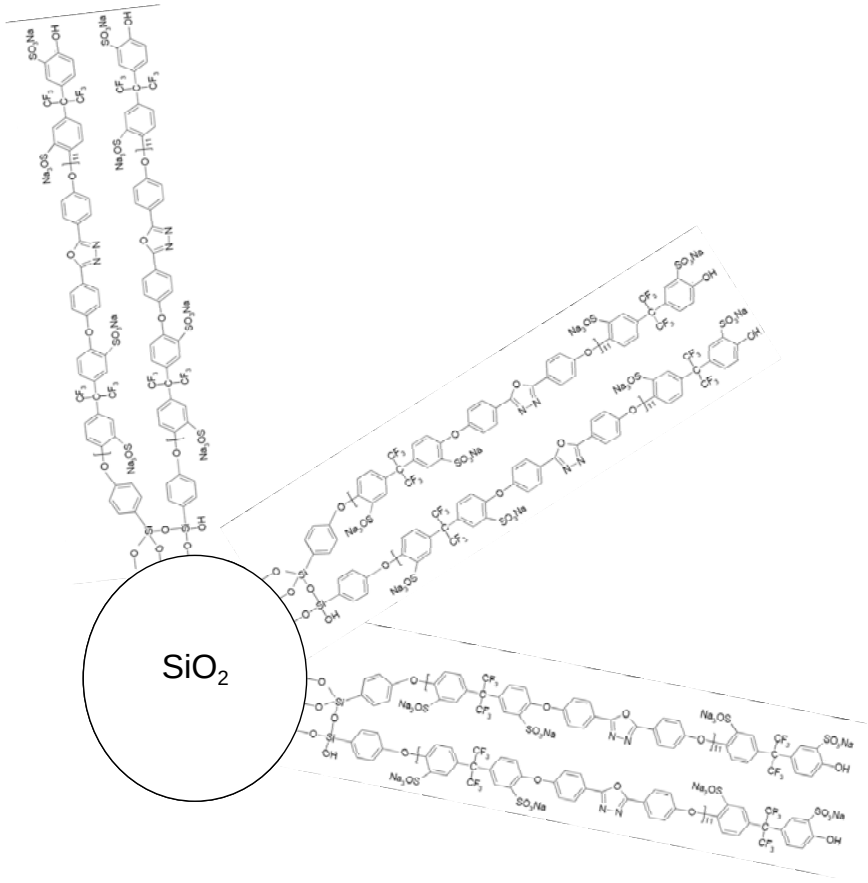
Figure 5: SEM images of the nanocomposite prepared with the functionalized silica

Figure 6: Dependence of proton conductivity on the temperature for the poly(hexafluor propane-1,3,4-oxadiazole) membranes for relative humidity equal to 100 %.

Figure 7: Proposed interactions between the polymer and H_3PO_4 (where the colors correspond to: blue carbon, navy nitrogen, yellow fluorine, green phosphorus, red oxygen, white hydrogen).

Figure 8: Proton conductivity of poly(hexafluor propane-1,3,4-oxadiazole) membranes as a function of the relative humidity and temperature.

Figure 9: FTIR spectra of the poly(hexafluor propane-1,3,4-oxadiazole) films in the region 4000 – 900 cm^{-1}.



Functionalized silica

(Scheme 1)

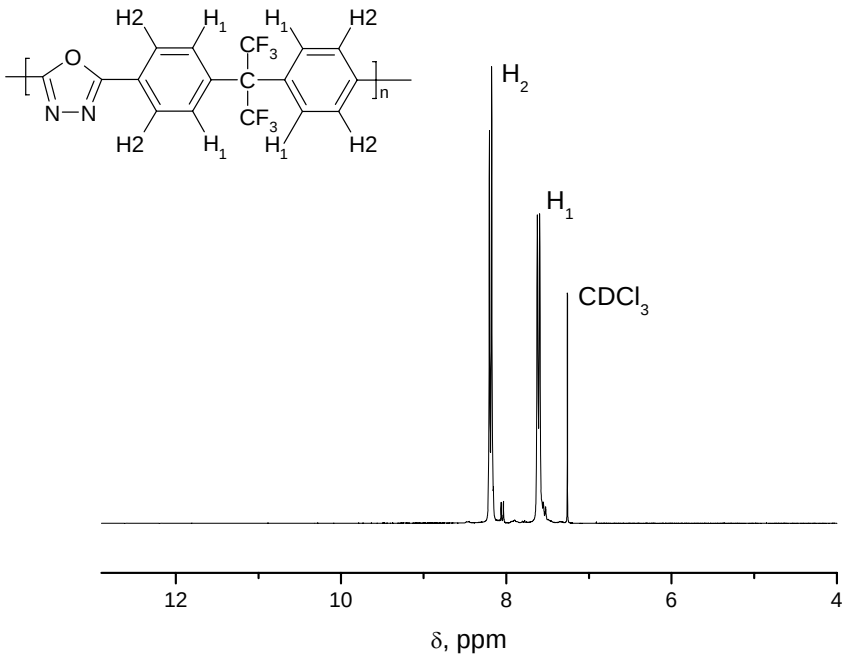
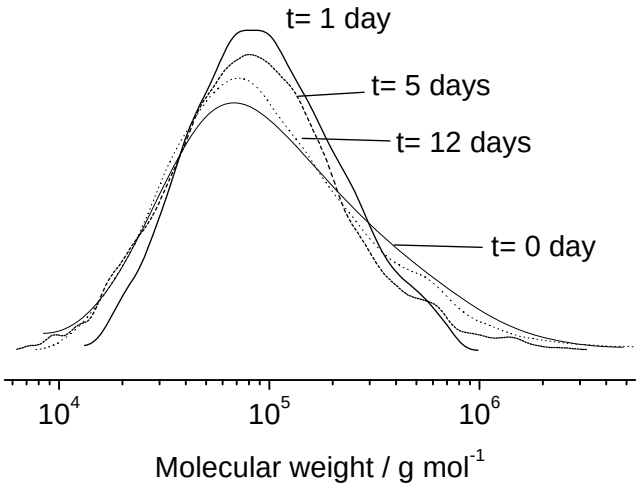
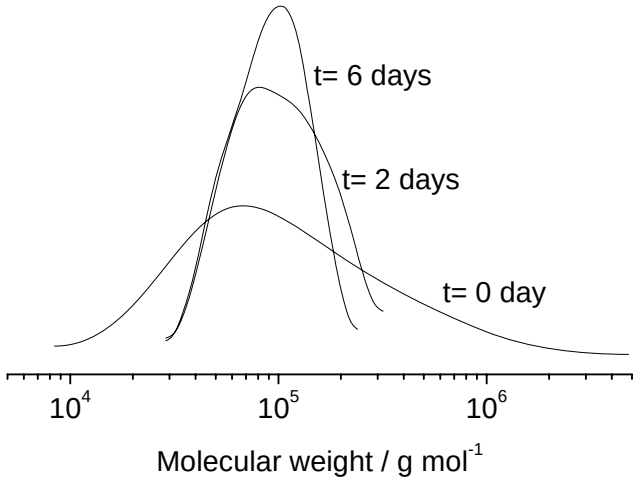


Figure 1


t= 1 day
t= 5 days
t= 12 days
t= 0 day
10^4
10^5
10^6
Molecular weight / g mol^-1

(a)


t= 6 days
t= 2 days
t= 0 day
10^4
10^5
10^6
Molecular weight / g mol^-1

(b)

Figure 2

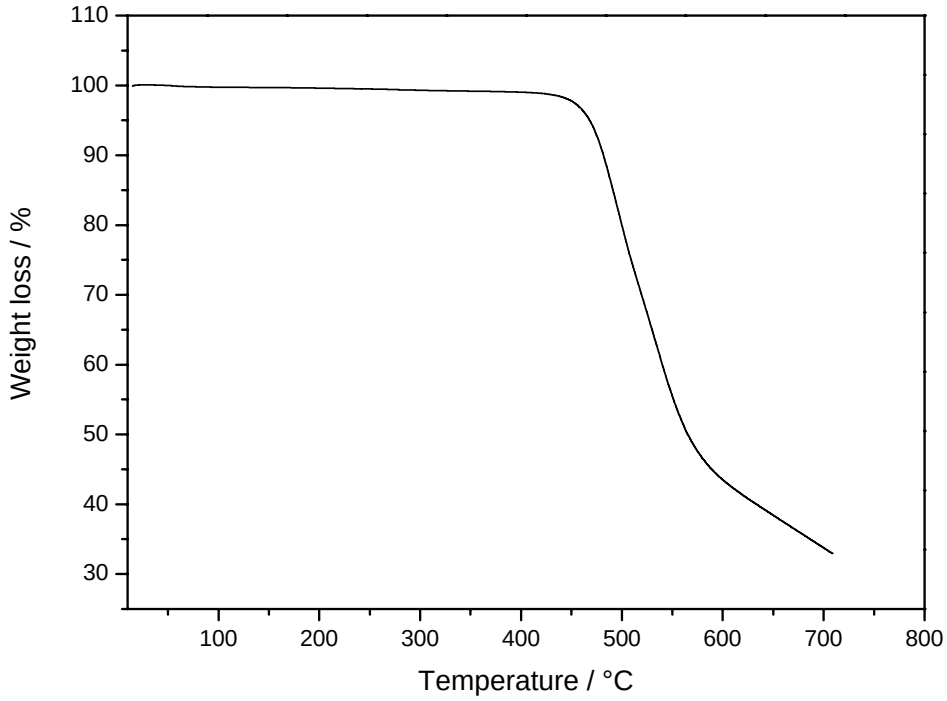

Weight loss / %
110
100
90
80
70
60
50
40
30
100
200
300
400
500
600
700
800
Temperature / °C

Figure 3

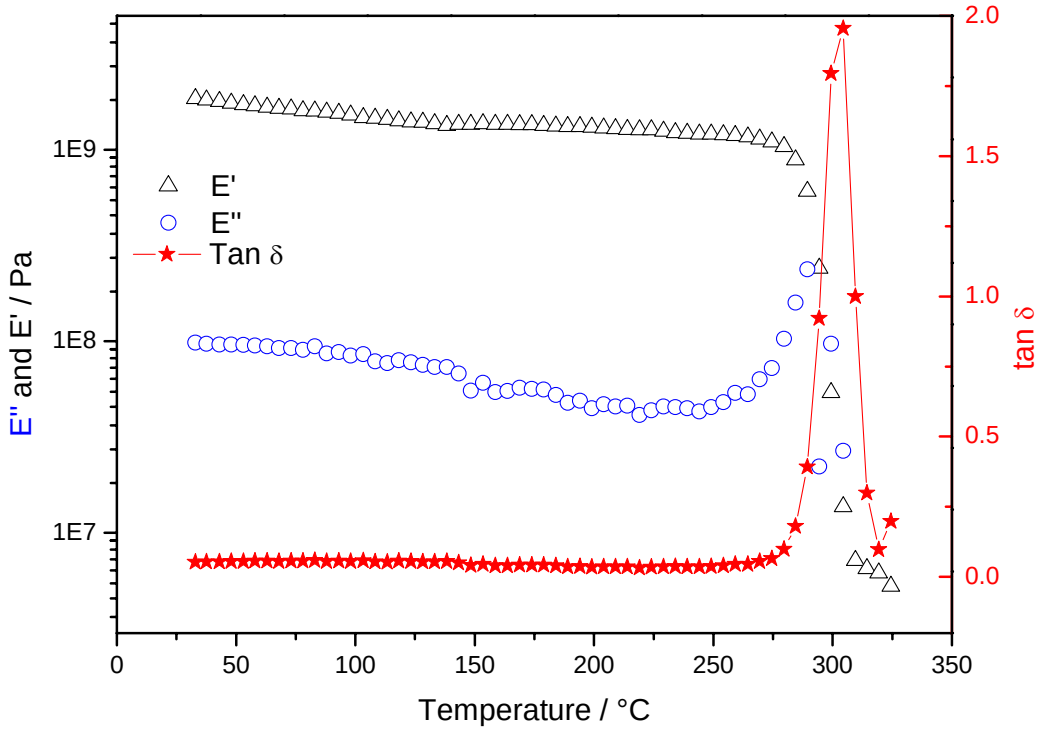
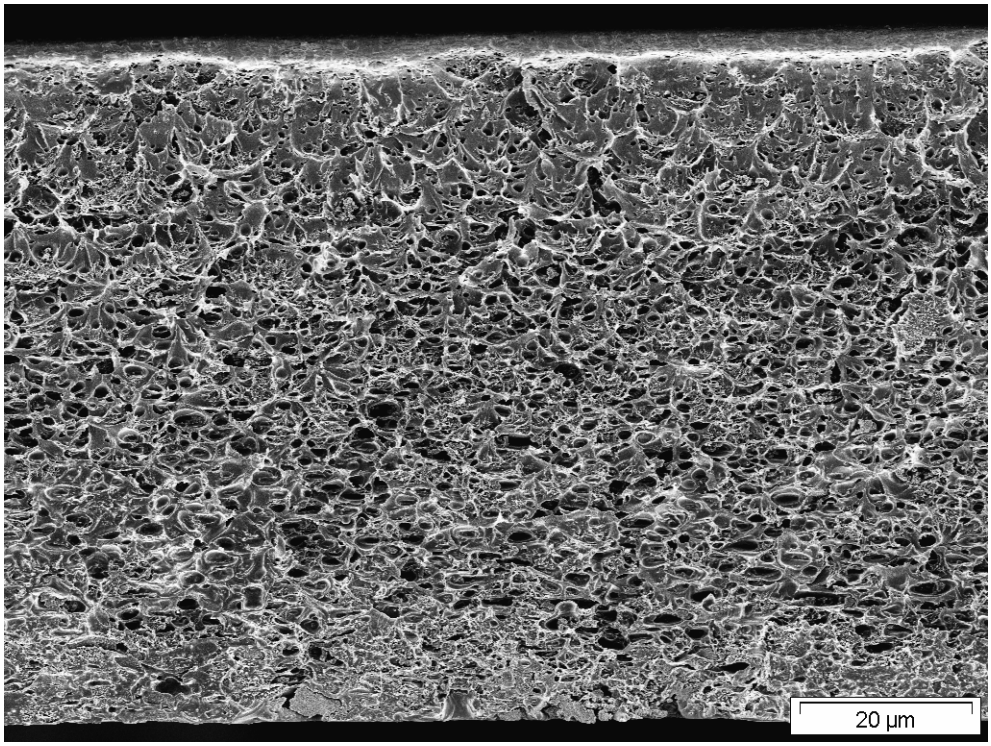

E'
E''
Tan δ
E'' and E' / Pa
tan δ
Temperature / °C
1E9
1E8
1E7
0
50
100
150
200
250
300
350
2.0
1.5
1.0
0.5
0.0

Figure 4



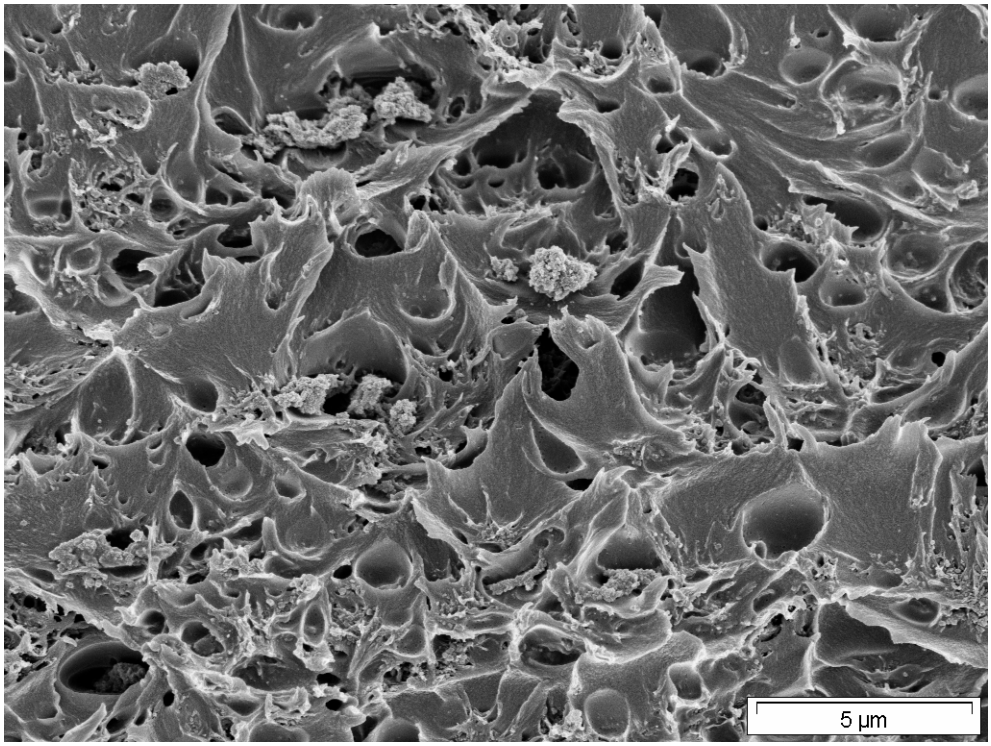


Figure 5

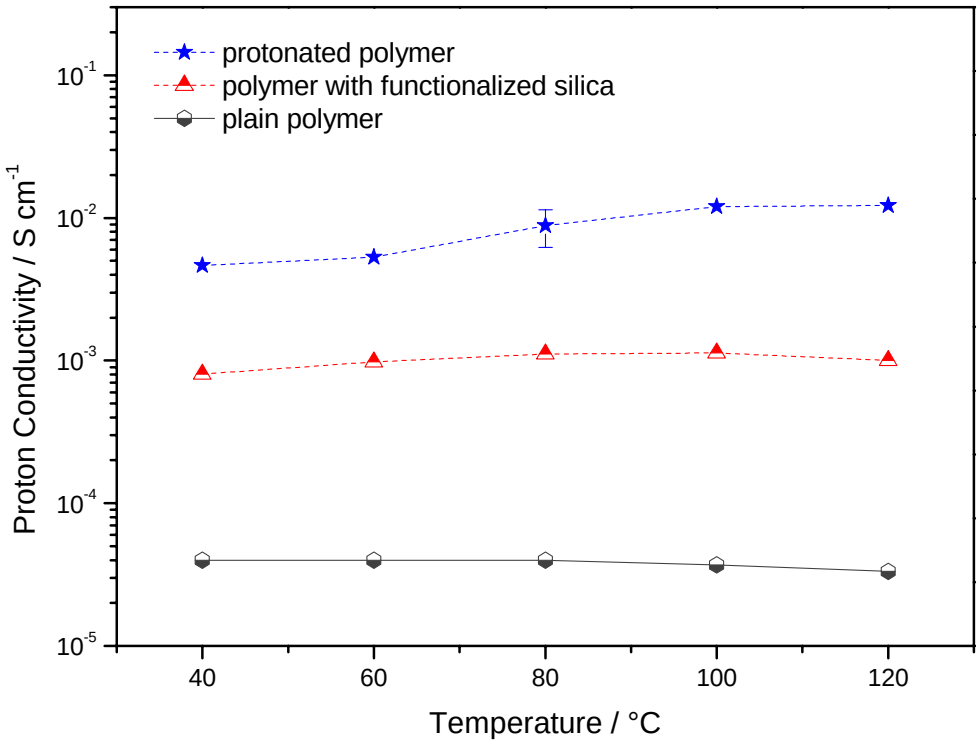

protonated polymer
polymer with functionalized silica
plain polymer
Proton Conductivity / S cm-1
10-1
10-2
10-3
10-4
10-5
40
60
80
100
120
Temperature / °C

Figure 6

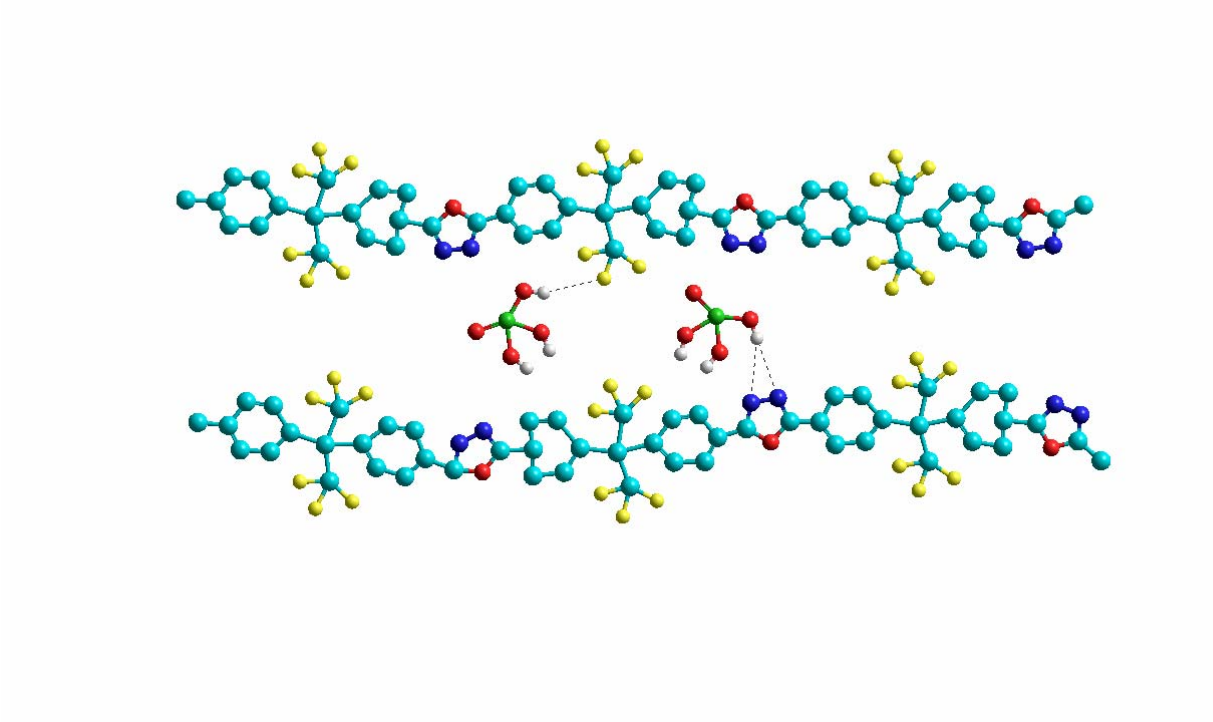


Figure 7

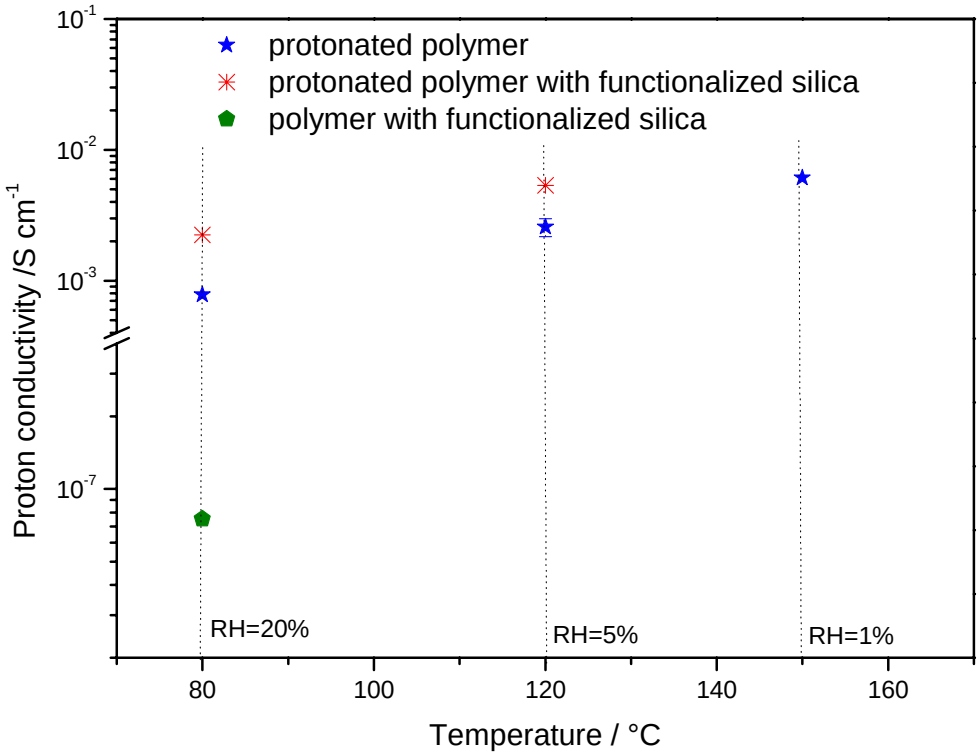

protonated polymer
protonated polymer with functionalized silica
polymer with functionalized silica
Proton conductivity /S cm-1
10-1
10-2
10-3
10-7
RH=20%
RH=5%
RH=1%
80
100
120
140
160
Temperature / °C

Figure 8

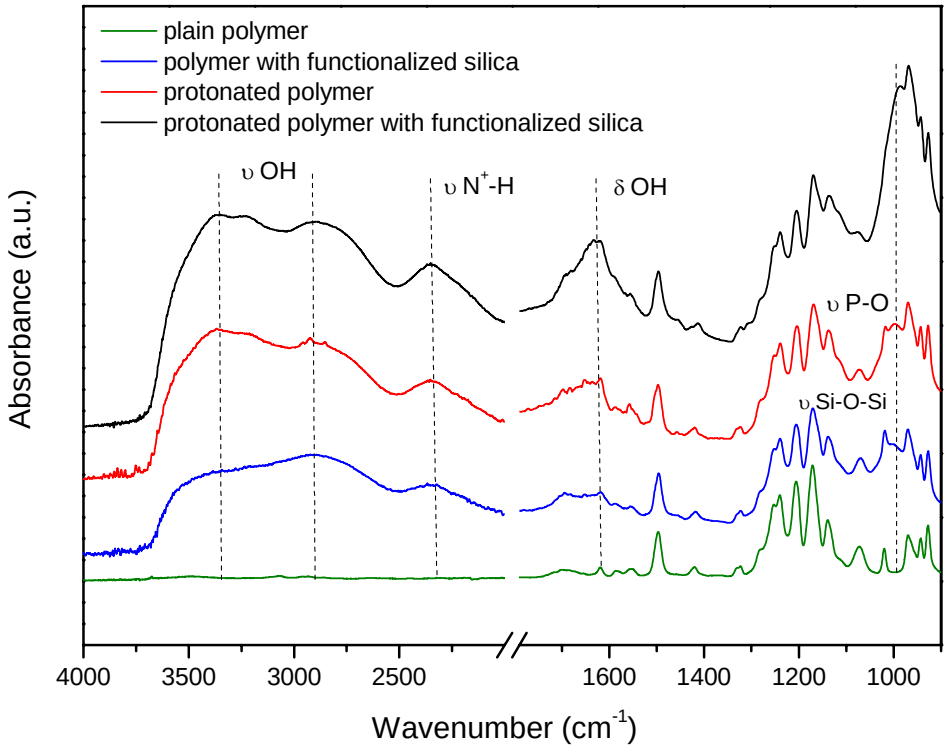

plain polymer
polymer with functionalized silica
protonated polymer
protonated polymer with functionalized silica
υ OH
υ N+-H
δ OH
υ P-O
υ Si-O-Si
Absorbance (a.u.)
4000
3500
3000
2500
1600
1400
1200
1000
Wavenumber (cm-1)

Figure 9