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Modification of Proton Conductive Polymer Membranes with Phosphonated Polysilsesquioxanes

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Abstract

New hybrid membranes for fuel cell applications based on sulfonated poly (ether ether ketone) (SPEEK) and phosphonated polysilsesquioxanes were synthesized. The impedance spectroscopy measurements show an increase of the proton conductivity for all studied composites, in comparison to plain SPEEK. For hybrid membranes containing 20 wt % of polysilsesquioxane with 80 mol % of phosphonated units the conductivities can reach values that are similar to Nafion 117 at 100 % RH. The best results of proton conductivity (142 mS/cm) were obtained for composites with 40 wt % of the same polysilsesquioxane at 120°C also at 100 % RH.

Keywords: fuel cells, hybrid membrane, polysilsesquioxanes, SPEEK, proton conductivity.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) can achieve potentially high energetic efficiencies with lower environmental impact. PEMFCs can particularly compete against batteries and diesel generators in portable, backup and reserve power applications [1], and are expected to be implemented in the automotive industry reducing emissions and noise.

The most used commercial polymer electrolyte for PEMFCs is Nafion® (DuPont), which is known for its high proton conductivity in the humid state and good chemical and mechanical stabilities at moderate temperatures. However, this perfluorinated polymer is very expensive and its properties deteriorate at temperatures above 100°C [2]. The automotive industry currently focuses on the application of fuel cells at temperatures near 130°C at lower humidity levels to simplify cooling and reduce problems of catalyst poisoning by CO, as well as to work in a condition of more favorable kinetics. For these operation conditions new membranes must be developed. The most discussed approach is based on polybenzimidazole membranes containing phosphoric acid. Among other approaches the use of phosphonated materials is under consideration for a long time [3, 4], however still with limited success [5]. In this scenery, phosphonated organic-inorganic hybrid materials, for example functionalized polysiloxanes, are promising candidates for intermediate temperatures (up to 200°C) and low humidity operations, due to its superior thermal and oxidative stability and elevated proton conductivity even in quasi-anhydrous conditions [6, 7].

A comprehensive study of sulfonic, phosphonic and imidazole as protogenic groups for PEMFCs has been recently reported [8] taking in account experimental data of model compounds. The comparison of limits and potential for each group showed an advantage for phosphonated compounds, due to its satisfactory proton conductivity and stability over a wider range of temperatures and humidities (even in water-free environments). Because of the hydrogen bonding and amphoteric properties of the phosphonic acids, membranes containing

phosphonated compounds could transport protons through structure diffusion, under low-humidity conditions, or through the dynamics of water, at high water contents [6]. It is also believed that phosphonic acid groups can keep the water better than sulfonic acid groups [3]. Furthermore, due to the strength of the carbon-phosphorus bond, these compounds are highly stable under hydrolytic conditions and/or high temperatures [6].

The various synthesis approaches of polymers containing phosphonic acid groups were recently reviewed in the literature [5]. A careful design of the way the phosphonic acid groups are attached to the polymer is required to provide the conditions necessary for an efficient proton transfer, i.e., formation of percolating hydrogen bonded networks for low-humidity conditions or a percolating network of water-filled channels for wet conditions. Nevertheless, it is known that polymer phosphonation in general is more difficult than the corresponding sulfonation.

Polymers with mixed functionalization obtained by sulfonation of previously phosphonated polymers were also reported [5]. It was found that the pure phosphonated polymers had higher thermal stability than polymers with similar sulfonation degree, but the proton conductivity was slightly lower.

The introduction of easily prepared phosphonated polysilsesquioxanes into organic polymer membranes to form a semi-interpenetrating network could provide a suitable proton-conducting structure, avoiding the usually complex procedures to get a well-designed phosphonated polymer.

Sol-gel processes are an interesting approach for the preparation of phosphonated polysilsesquioxanes. These processes allow adjusting the degree of interpenetration of organic and inorganic networks on an atomic scale. Polysilsesquioxanes can be synthesized using organoalkoxysilanes $R'_xSi(OR)_{4-x}$ (R' =alkyl, phenyl) as precursors, which lead to the formation of organic-inorganic hybrid compounds [9]. The ligand R acts as a network modifier in the resulting structure. Here, diethylphosphatoethyltriethoxysilane (Ph-TEOS)

represents an interesting molecular precursor, since no cleavage of the Si-C and P-C bonds is observed under hydrolytic, basic, or acidic conditions [10]. Pure polyorganosiloxanes are normally not suitable to prepare flexible and self-standing membranes, but semi-interpenetrating networks of bridged polysilsesquioxanes into organic polymer matrices, preferentially high performance polymers with intrinsic proton conductivity, could provide very suitable membranes for fuel cell applications. They can be prepared by solution blending, followed by membrane casting and further treatment to ensure the network formation [11].

Sulfonated polymers (e.g., sulfonated poly (ether ether ketone), SPEEK [12-14], or sulfonated polysulfone, SPSU [15,16]) have been frequently investigated as organic polymer matrices for application in PEMFCs, having at intermediate degrees of sulfonation a satisfactory proton conductivity and chemical resistance. SPEEK has been extensively used in our group [17-23], being reported as a low cost alternative membrane mainly for direct methanol fuel cells (DMFC). A number of publications describe the modification of SPEEK membranes with inorganic fillers, as zirconium phosphate [21, 24], silica [25], sulfonated silica [17], heteropolyacids [22, 26], and nanoclays [27]. These modifications have been carried out mainly to suppress methanol permeation while keeping proton conductivity. However, when considering the application for hydrogen fuel cell like most sulfonated polymers, they dehydrate above 100°C and also have reduced proton conductivity at low humidity levels.

The main objective of this work is the preparation and characterization of novel organic-inorganic composite membranes from sulfonated poly (ether ether ketone) and phosphonated polysilsesquioxanes for proton conductivity at conditions at which SPEEK alone is not good enough. The membranes were prepared by a controlled sol-gel route involving co-condensation of phosphonic modified silane and tetraethoxysilane (TEOS) precursors and a semi-interpenetrating network was achieved by posterior acid treatment of the hybrid membranes. The water uptake and proton conductivity properties of the composite

membranes were investigated and compared with the plain SPEEK membrane. The membranes were also characterized by infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), atomic force microscopy (AFM), and scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

Poly (ether ether ketone) (PEEK) 450 PF powder form was purchased from Victrex and dried under vacuum at 90°C overnight before use. Sulfuric acid 95-97% from Merck, tetraethoxysilane (TEOS) for synthesis from Gelest, diethylphosphatoethyltriethoxysilane (Ph-TEOS) 95% from Gelest, dimethylsulfoxide (DMSO) 99% from Merck, ethanol absolute from Merck, and hydrochloric acid 37% from Merck were used as received.

2.2. PEEK sulfonation

Sulfonated poly (ether ether ketone) (SPEEK) with sulfonation degree of ca. 50% was prepared by the following procedure. Ten grams of PEEK were dissolved in 500 mL of concentrated sulfuric acid and vigorously stirred at room temperature for 48 h. Then, the polymer solution was gradually precipitated into ice-cold demineralised water under stirring. The polymer precipitate was filtered, washed several times with distilled water, and left to settle overnight in demineralised water. Afterwards, the polymer was repeatedly washed, until the pH of the washing solution was neutral, and dried for 12 h in vacuum at 80°C. The sulfonated polymer showed a distinct yellow coloration. The sulfonation degree was determined by elemental analysis, as described by Nolte et al [28].

2.3. Synthesis of phosphonated polysiloxanes

Polymerization and hydrolysis of Ph-TEOS

Two grams (6.1 mmol) of Ph-TEOS (Scheme 1) were dissolved in 10 mL of ethanol. While stirring, 0.5 mL of 0.1 mol·L⁻¹ hydrochloric acid was added drop wise. After 6 days the solvent was removed in a rotary evaporator (at 200 mbar), and the viscous liquid product was dried under vacuum at 60°C until constant weight. The reaction in the presence of diluted acid leads to the formation of polysilsesquioxanes with phosphonic groups in the ester form. In order to bring the groups to the acid form a hydrolysis at more aggressive conditions in concentrated acid is then required.

Ca. 1.7 g of the oligomer was further hydrolyzed by the addition of 30 ml of 37 wt% hydrochloric acid prior to stirring at 120°C for 16 h (procedure based on Steininger et al. [29]). After cooling, hydrochloric acid was removed in a rotary evaporator and the resulting transparent light yellow ductile solid was repeatedly dissolved in water and dried in vacuum to remove any residues of the acid. Afterwards, the solid was dried at 80°C for 24 h, containing now acid phosphonic groups.

INSERT Scheme 1 HERE

Copolymerization of Ph-TEOS and TEOS

Partially functionalized polysiloxanes with compositions ranging from 90/10 to 10/90 (mol of phosphonic functionalized/ mol of non functionalized segments) were synthesized by a procedure based on that described by Carbonneau et al. [9]. The reagents Ph-TEOS and TEOS in the appropriate molar ratio (ca. 5 g total mass) were dissolved in 30 mL of absolute ethanol and, under stirring, 2 mL of HCl (0.1 mol·L⁻¹) were added as catalyst. The homogeneous mixture was maintained under constant stirring for time periods from 3 to 6 days, depending

on the composition. After this period, the solvent and excess monomers were removed in a rotation evaporator. A clear viscous liquid, soluble in THF, NMP and DMSO, was obtained for all compositions. The obtained partially functionalized polysilsesquioxane contained phosphonic groups in the ester form.

2.4. Preparation of the SPEEK composite membranes

Three strategies were followed to prepare membranes:

(1) Mixture of SPEEK and Ph-TEOS oligomers with acid phosphonic groups

SPEEK (50% of sulfonation degree) was first dissolved in DMSO leading to a final concentration of 7 wt%. The Ph-TEOS polysilsesquioxane (with phosphonic groups already in the acid form) was separately dissolved in DMSO. The two solutions were mixed to a final proportion of 20 wt% of polysilsesquioxane to SPEEK. This solution was stirred for at least 12 h and cast at 60°C for solvent evaporation on a glass plate, which was previously hydrophobised with octadecyl trichlorosilanes. All the membranes were transparent, flexible and self-standing, with an average thickness of 50 µm.

(2) Mixture of SPEEK and copolymers of Ph-TEOS and TEOS with acid phosphonic groups

Ph-TEOS/TEOS copolymers with ester groups (0.50 g) were treated with concentrated HCl (50 mL) under reflux for 24 h to hydrolyze the phosphonic ester groups to the acid form. The mixture was filtered through a fritted funnel and washed with excess H₂O to remove all traces of HCl, and then with ethanol. The residue, which in this case is a white fine powder, was dried under vacuum at 120°C for 24 h. In this case, the insoluble acid powder material was well dispersed in the polymer solution by vigorous stirring. The membranes were cast as described in the previous section.

(3) Mixture of SPEEK and Ph-TEOS/TEOS copolymers with phosphonic groups in the ester form followed by hydrolysis

Appropriate amounts of Ph-TEOS copolymers containing phosphonic groups in the ester form were added to 7 wt% SPEEK solutions in DMSO. The obtained solutions were stirred for at least 12 h and cast at 60°C for solvent evaporation on hydrophobised glass plates. After that the obtained membranes were dried under vacuum at 80°C for 24 h.

The membranes were then submitted to different treatments in order to hydrolyze the diethylphosphonate groups to the phosphonic acid and to promote the formation of a bridged polysilsesquioxane network in the organic matrix. Three approaches were tested. In the first one, the membrane was treated with concentrated hydrochloric acid at 60°C for 24 h. In the second treatment the membrane was kept under reflux at 110-120°C in concentrated hydrochloric acid for 24 h. In the third approach the membrane was treated with trimethylbromosilane (TMBS) at 60°C for 24 h and then with H₂O for 24 h at 60°C [9]. After the acid treatments the membranes, initially transparent, became opaque with a pearl brightness. In all the cases the membrane was washed in water during at least 1 week after the hydrolysis.

2.5. Characterization of the composite membranes

Proton conductivity measurements

Proton conductivity was measured by the AC impedance spectroscopy in the frequency range of 10-10⁶ Hz at signal amplitude of ≤ 100 mV, and calculated from the impedance modulus at null phase shift (high frequency side). The impedance measurements were carried out on membrane stacks with cumulative thickness around 500 μm . The proton conductivity of the samples was determined at temperatures ranging from 30 to 120°C. Most of the experiments were made at 100% relative humidity. In this case, the measurement was performed using a

stainless steel sealed-off cell, consisting of two cylindrical compartments connected by a tube. One compartment contained water, while the other compartment housed the membrane under test. Some experiments were carried out at controlled lower humidities. In this case the 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.

Swelling measurements

For the swelling studies the membrane samples were dried in a vacuum oven at 90°C overnight. After drying, the samples were weighed and immersed in deionized water or 20 wt% aqueous methanol solution and equilibrated for 24 hours at room temperature or at 60°C. The weights of the swollen membranes were measured after carefully removing the water from both surfaces. Membrane swelling (wt %) was evaluated calculating the difference between the wet and the dry weight and dividing by the dry weight.

Membrane Morphology

The cryo-fractured surfaces (cross-sections) of the membranes were analyzed by scanning electron microscopy in a LEO 1550VP equipment with a Gemini field emission column. The samples were coated mainly with Au/Pd to obtain images with secondary electrons.

Tapping mode atomic force microscopy (AFM) was performed with a VEECO NANOSCOPE 4 Surface Probe Microscope.

Spectroscopic Characterization

FTIR spectra from dried membranes were recorded on a Bruker Equinox IFS 55 spectrometer (ATR mode) in the range 400-4000 cm^{-1} . ^{29}Si MAS NMR (59.6 MHz) spectra were recorded on a Bruker DMX-300 instrument with a pulse width of 4 ms and a pulse delay of 100 s.

Thermal Analyses

Thermogravimetric analysis (TGA) experiments were carried out in a Netzsch 209 TG, equipped with a TASC 414/3 thermal analysis controller or in a Netzsch STA 449C equipment. The samples (about 8–10 mg) were heated from 50 to 1000°C under nitrogen atmosphere at 10°C/min.

3. Results and Discussion

3.1. Synthesis and characterization of phosphonated polysiloxanes

Phosphonic acid modified silica materials obtained using copolymerization of suitable precursors by sol-gel methods have been reported since 1996 by different authors from the fundamental point of view [9,30] and for different applications, such as non-linear optical devices [31], supported catalysts [10], and proton conductors [29,32]. Like in most of the mentioned papers, here in this work hybrid organic-inorganic materials with covalently bonded phosphonates were synthesized by using the acid-catalyzed sol-gel procedure. Further hydrolysis of the phosphonate moiety was generally performed by refluxing in 37% HCl for 24 h. In view of the literature, the cleavage of diethylphosphonate ester groups on silica seems to be best performed by using harsh conditions (Scheme 2). The usual treatment involves the reflux in concentrated HCl. Cardenas [30] and Aliev (10) have described the gelation of Ph-TEOS catalyzed by HF and HCl, respectively.

INSERT Scheme 2 HERE

The infrared spectra of Ph-TEOS and acid Ph-TEOS are shown in Figure 1. For Ph-TEOS, two strong peaks due to the asymmetric (1050 cm^{-1}) and the symmetric (768 cm^{-1}) P-O-C

stretching, together with the doublet at 1026 and 1074 cm^{-1} of Si-O-C asymmetric stretching, are characteristic [33]. The bands corresponding to Si-O-Si groups are present in the spectrum of acid Ph-TEOS oligomers, confirming the condensation of Ph-TEOS units. The band centered at 1000 cm^{-1} is attributed to the asymmetric stretching vibration in Si-O-Si groups, while the small peak at 810 cm^{-1} is due to symmetric stretching of these groups. The broad band at 3100-3500 cm^{-1} is assigned to the O-H stretching of silanol groups and adsorbed water. The presence of some unreacted Si-OH groups is confirmed by the strong signature band at ca. 930 cm^{-1} in acid Ph-TEOS oligomers spectrum [34]. The hydrolysis of the diethylphosphonate groups to the phosphonic acid can be clearly detected by the new band at ca. 2280 cm^{-1} , very characteristic of phosphonic acid groups [33], and by the disappearance of the strong P-O-C band at 1050 cm^{-1} .

INSERT Figure 1 HERE

^{29}Si CP MAS NMR spectroscopy can be used to quantitatively measure the degree of condensation (extent of reaction). In the case of the acid Ph-TEOS oligomers (Figure 2), the classical T resonances (SiO_3 units) are present [35]. The spectrum shows a major T^3 peak at -69 ppm attributed to SiO_3 groups possessing 3 siloxane bridges. The minor signal at -60 ppm corresponds to SiO_3 groups possessing 2 siloxane bridges (T^2) [30], while the small peaks at -103 and -112 ppm can be attributed to Q^3 and Q^4 signals (SiO_4 units possessing 3 and 4 siloxane bridges, respectively). The latter two Q signals were unexpected for a trifunctional silane, and could be attributed to impurities or to some cleavage of Si-C bonds. No direct evidence of cyclic products was found as suggested for similar bifunctional silanes [29]. From the results a degree of condensation of approximately 90% was estimated, i.e., the final product was almost a completely branched polysilsesquioxane.

INSERT Figure 2 HERE

The condensation species of a 1/10 (molar ratio) Ph-TEOS/TEOS copolymerization monitored by ^{29}Si NMR spectroscopy is shown in Figure 3. Cleavage of the phosphonate ester was performed on the copolymers by using concentrated HCl at 110°C . The copolymerized material has resonances consistent with T and Q environments in the ratio $\text{T/Q} = 0.1$, as expected, indicating that there was no Si-C bond cleavage. The Q^4 signal (-113 ppm) was the major one indicating that the formation of a silica network occurred.

INSERT Figure 3 HERE

^{31}P NMR (Figure 4) confirms the acid hydrolysis. The starting material, Ph-TEOS/TEOS copolymers in the ester form, presents only one symmetric signal at ca. 35 ppm indicating a homogeneous environment of the phosphonate ester. The acid treatment modified the spectrum and after that the copolymers presented two significant signals at 33.4 and 24.3 ppm which were respectively attributed to the free phosphonic acid group (PO_3H_2) and to the phosphonic acid bonded to silicon atoms ($\text{O}=\text{P}(\text{OSi})_2$) [9].

INSERT Figure 4 HERE

3.2. Membrane preparation and characterization

Polysilsesquioxanes functionalized with phosphonic acid groups have been considered for application as proton conductors before [29, 32]. However the use of proton conductive materials for fuel cell application requires not only high proton conductivity but the membranes must have a reasonable mechanical stability, being flexible enough to stand the

usual processes of manufacture into membrane-electrode-assemblies. For this reason in this work the functionalized polysilsesquioxane was blended with SPEEK. SPEEK gives a better mechanical stability to the phosphonated polysilsesquioxane phase, which otherwise would be brittle and not stable enough.

SPEEK with a degree of sulfonation of 50% was selected for this study because this degree of substitution by sulfonic acid groups combines reasonable proton conductivity with insolubility in water. The FTIR spectrum of the sulfonated PEEK prepared and used in this work is shown in Figure 5. The spectrum is very similar to others already reported in literature [12,13], showing the additional absorption bands associated with sulfonic acid groups at 3440 (ν O-H of \sim SO₃H and absorbed water), 1251 (ν_{as} O=S=O), 1078 (ν_s O=S=O), 1021 (ν S=O) and 708 cm⁻¹ (ν S-O). The sulfonation can also be confirmed by the split of the aromatic C-C absorption band at 1490 cm⁻¹, with the appearance of a new band at 1471 cm⁻¹, and of the absorption band at \sim 1414 cm⁻¹, with a new band at 1402 cm⁻¹. The relative intensities of the bands at 1490 and 1471 cm⁻¹ [13] are consistent with the sulfonation degree calculated by elemental analysis.

INSERT Figure 5 HERE

Membranes obtained from the mixture of SPEEK and Ph-TEOS oligomers with acid phosphonic groups

The membranes obtained after addition of up to 20 wt % Ph-TEOS oligomers in SPEEK were transparent, flexible and quite resistant to manipulation. Impedance spectroscopy results show that for the SPEEK membrane with 20 wt % acid oligomers the proton conductivity is enhanced in about 27% in relation to plain SPEEK in the temperature range from 30 to 80°C (Figure 6).

INSERT Figure 6 HERE

Figure 7 shows SEM images of this hybrid membrane. The top layer is richer in the inorganic polymer. The presence of two distinct phases is clearly observed. It is important to note that in Ph-TEOS oligomers the phosphonic groups are already in the acid form (the diethylphosphonate group was hydrolyzed to the phosphonic acid) and no TEOS was added to the mixture. Therefore a very low crosslinking level is expected and the mobility of the system is high enough to lead to a macroscopic phase separation during the membrane formation.

INSERT Figure 7 HERE

It was indeed detected that, after some pervaporation experiments with aqueous methanol solutions, the top layer, which should be richer in the inorganic oligomer is completely removed and holes are formed in the SPEEK-rich sub layer. This is related to the high solubility of this phosphonated oligomer in polar solvents.

In order to fix this problem, the Ph-TEOS monomer was copolymerized with a more functionalized silane, TEOS, to obtain copolysilsesquioxanes with a reduced solubility in polar solvents.

Mixture of SPEEK and copolymers of Ph-TEOS/TEOS with acid phosphonic groups

When TEOS was copolymerized with Ph-TEOS and further hydrolyzed with concentrated acid to give free phosphonic acid groups before preparing the membrane in analogy to the first procedure, an insoluble functionalized polysilsesquioxane is obtained, due to additional crosslinks. Only a dispersion of the inorganic component in the SPEEK solution is possible and the final membrane is not homogeneous (see Figure 8). Another strategy was then chosen

to obtain homogeneous membranes.

INSERT Figure 8 HERE

Mixture of SPEEK and Ph-TEOS/TEOS copolymers with phosphonic groups in the ester form followed by hydrolysis

After the polycondensation of Ph-TEOS and TEOS a copolymer, which is still soluble in solvents used for membrane preparation (e.g. DMSO), is obtained. A clear solution containing both SPEEK and the polysilsesquioxane is achieved, leading to a clear homogeneous film after solvent evaporation.

Most of the results were obtained with copolymers prepared with 20 mol% TEOS and 80 mol% Ph-TEOS and a condensation time of 5 days. The copolymer is still soluble in DMSO. Membranes with 5, 10, 15 and 20 wt % of this copolymer mixed with SPEEK were prepared with no apparent phase separation. Figure 9 shows SEM micrographs of a blend containing 20 wt % of the 80/20 (molar ratio) Ph-TEOS/TEOS copolymer still in the ester form.

INSERT Figure 9 HERE

To liberate the phosphonic acid groups and to obtain a semi-interpenetrating network of the polysilsesquioxane with acid phosphonic groups in SPEEK, the membrane was submitted to different treatments. In the first one, following procedures from literature for hydrolysis of diethylphosphonate groups [10], the membrane was refluxed at ca. 110°C in concentrated HCl for 24 h. To test a milder condition, the membrane was treated also with concentrated acid at 60°C in a closed vessel for 24 h. An alternative way to carry out the hydrolysis under much milder conditions is the use of trimethylbromosilane (TMBS), to proceed the trimethylsilylation of the phosphonic group, followed by the release of trimethylsilane groups

by neutral water [9]. Beside the hydrolysis of the phosphonic groups, all the post treatments probably also contribute to complete the hydrolysis of the silane groups, increasing the crosslinking of the inorganic phase. Attempts to quantify the crosslinking in the membrane by ^{29}Si NMR did not succeed since the signal is diluted due to blending with the SPEEK matrix. The morphology of the samples submitted to the different methods for converting diethylphosphonate to the phosphonic acid is shown in Figure 10.

INSERT Figure 10 HERE

It is observed that the treatment with TMBS promotes the formation of a thin superficial layer (ca. 300 nm) on the membrane, while no top layer is achieved with hydrochloric acid treatments. This is related to the fact that protons from HCl can diffuse through the membrane to promote a semi-interpenetrating network, but the TMBS, a relatively large molecule, acts just on the membrane surface.

Characterization by Atomic Force Microscopy

In order to better differentiate phases in the membrane before and after the hydrolysis, atomic force microscopy was used. The morphology of the membrane surface was investigated using tapping mode allowing obtaining both height and phase contrast images. The AFM phase contrast images are summarized in Figure 11. Phase contrast can provide nanometer-scale information about the surface structure, going beyond simple topographical mapping to detect, among other properties, variations in composition and regions of high and low hardness. This is particularly useful for systems like those investigated here, in which one phase is inorganic and significantly harder than the organic matrix.

There is a marked change in the phase contrast images when the samples are submitted to different hydrolytic treatments. Whereas the image corresponding to the non-treated

membrane shows a rough phase separation, the other images contain a fine grainy structure. Among the treated samples, those submitted to the harsh treatment with HCl at 110°C have a rougher structure [36]. The other two images, from samples submitted to milder hydrolysis conditions, show a much finer structure. Membrane treated with HCl at 60°C has a very well defined morphology, suggesting phase separation in nanodomains, with the inorganic domains well distributed all over the sample.

It seems that sample treated with HCl at 60°C presents a better connectivity between dark regions, forming a percolated ionic transport pathway, which might result in higher proton conductivities.

INSERT Figure 11 HERE

Figure 12 quantifies the size distribution of domains in phase contrast AFM micrographs of the membranes with different inorganic contents before the hydrolysis of the phosphonic group. A diagonal line was traced in each micrograph and the occurrence of each domain size along the line was analyzed.

A periodic structure of ca. 25 nm is observed in the plain SPEEK membrane. This structure can result from regions which are differentiated by higher sulfonated levels. Kim et al. [37] detected domains in the range up to 50 nm for sulfonated polysulfones investigated at 50% relative humidity, which they attributed to differences in hydrophilicity. More hydrophilic domains absorb water becoming softer, while more hydrophobic regions are stiffer. With the incorporation of inorganic phase, domains in the size range of 60 nm could be detected with increasing occurrence as the inorganic content increases.

INSERT Figure 12 HERE

Proton conductivity

The proton conductivity values of the composite membranes containing 20 wt% of 80/20 (molar ratio) Ph-TEOS/TEOS copolymers, in the temperature range of 30-80°C, are given in Fig.13. Before the measurements, all the acid treated membranes were stored in deionized water for at least one week, with frequent water replacements, as it was noted that very high conductivities can be measured just after the treatment, but a stable value is obtained only after several days in water. Nafion 117® was also characterized in the same conditions. All the hybrid membranes had higher conductivity values than the plain SPEEK, and all membranes exhibited an increase in proton conductivity with increasing temperature. The membrane treated with HCl at 60°C reached a value near 80 mS/cm at 80°C, close to the value for Nafion 117® (84 mS/cm).

INSERT Figure 13 HERE

Comparing the different methods to promote hydrolysis of diethylphosphonate groups, it is noted that the best treatment is under milder acidic conditions, i.e., heating the membrane in 37% HCl at 60°C. This method proved to be effective to release the phosphonic groups without deterioration of the SPEEK matrix. The TMBS treatment is much milder, but, as already mentioned, it is probably working only in the most superficial layer of the membrane. Therefore, great parts of the phosphonic groups in the bulk of the membrane are not available for proton conduction, which explains the lower conductivity.

It is worth mentioning at this point that the water uptake of the membrane treated with HCl at 60°C is, at room temperature, slightly lower for the composite membrane (13 wt% water uptake) than for plain SPEEK (19 wt% water uptake).

The influence of the phosphonated 80/20 (molar ratio) Ph-TEOS/TEOS copolymer concentration in SPEEK membranes was also studied. Figure 14 shows the results for

membranes treated with HCl at 110°C. It is observed that the proton conductivity increases markedly with the increase in the phosphonated polysilsesquioxane concentration.

INSERT Figure 14 HERE

As expected the addition of a phosphonated compound resulted in higher proton conductivity, because of the pronounced amphoteric character of the phosphonic acid leading to higher charge carrier concentrations and, therefore, higher conductivities [8].

Another set of experiments was carried out to investigate the behavior of SPEEK membranes with 80/20 (molar ratio) Ph-TEOS/TEOS copolymers now treated with HCl at 60°C. In this case the proton conductivity measurements were conducted up to 120°C (Figure 15). A better performance at the high tested temperatures (up to 120°C) was confirmed. The composites are quite stable and mechanically strong in these conditions.

INSERT Figure 15 HERE

A significant increase of proton conductivity values is observed when the 80/20 (molar ratio) Ph-TEOS/TEOS copolymer content goes to 40 wt%. This high proton conductivity can be attributed to a well-developed percolation of the phosphonated phase.

Measurements at controlled humidities were carried out with some of the membranes with high proton conductivity at 100% RH. Figure 16 gives the proton conductivity data at 80°C for 60 and 42% relative humidities (RHs) for SPEEK membranes with 20 and 40 wt% of phosphonated polysilsesquioxane treated with HCl at 60°C. All the measurements were made after at least two hours in equilibrium with water vapor. The composite membranes retain proton conductivity in a more or less similar way as Nafion 117®. For 20% RH, the membrane with 40 wt% of polysilsesquioxanes has a proton conductivity of 7 mS/cm, 20-fold

smaller than at 100% RH, showing that transport in water-filled channels is the principal proton conduction mechanism in the composite membranes. Nevertheless, the conductivity values obtained at low humidity conditions (ca. 10^{-2} S/cm at 80°C and 20% RH) are quite good in comparison to other measurements reported in the literature for various membranes [6, 38-41].

INSERT Figure 16 HERE

Conclusions

Hybrid composite membranes were prepared from SPEEK and phosphonated polysilsesquioxanes for potential application in fuel cells. Copolysilsesquioxanes were obtained from a phosphonated silane and tetraethoxysilane by a modified sol-gel method and dispersed in SPEEK solutions. The flexible and transparent membranes cast from these solutions were then treated by different treatments in order to hydrolyze the diethylphosphonate groups to phosphonic acid and to form a silicate semi-interpenetrating network.

At 100% RH, the conductivities of the composite membranes increase with the increase of the amount of phosphonated groups. The proton conductivity reached a maximum (142 mS/cm) at 120°C with 40 wt % of polysilsesquioxane with 80 mol% of phosphonated units in SPEEK (SD = 50%), which was higher than that of Nafion 117® at the same conditions.

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Figure Captions

Scheme 1. Chemical structure of diethylphosphatoethyltriethoxysilane (Ph-TEOS).

Scheme 2. Condensation of Ph-TEOS and co-condensation of Ph-TEOS and TEOS, followed by hydrolysis of the phosphonate function.

Figure 1. FTIR spectra of Ph-TEOS and acid Ph-TEOS.

Figure 2. ^{29}Si CP MAS NMR spectrum of the condensation product of acid Ph-TEOS oligomers prepared under acidic conditions.

Figure 3. 1/10 (molar ratio) Ph-TEOS/TEOS condensation products, after acid hydrolysis, monitored by ^{29}Si NMR.

Figure 4. ^{31}P NMR spectrum of a Ph-TEOS/TEOS copolymer after treatment with concentrated hydrochloric acid.

Figure 5. FTIR spectrum of sulfonated PEEK.

Figure 6. Proton conductivity at 100% RH as function of the temperature: ■ plain SPEEK, ● SPEEK membranes with 20 wt % 80/20 (molar ratio) Ph-TEOS/TEOS copolymer.

Figure 7. SEM micrographs of SPEEK membranes with 20 wt % 80/20 (molar ratio) Ph-TEOS/TEOS copolymer prepared by casting.

Figure 8. SEM micrograph of SPEEK membranes with 20 wt % 80/20 (molar ratio) Ph-TEOS/TEOS copolymer, which was previously hydrolyzed and added to the SPEEK solution.

Figure 9. SEM micrographs of SPEEK membranes with 20 wt % 80/20 (molar ratio) Ph-TEOS/TEOS copolymer before hydrolysis.

Figure 10. SEM micrographs of SPEEK membranes with 20 wt % of 80/20 (molar ratio) Ph-TEOS/TEOS copolymer submitted to different hydrolysis treatments: (a) TMBS/H₂O, (b) 37% HCl at 110°C (c) 37% HCl at 60°C.

Figure 11. AFM phase contrast images of SPEEK membranes with 20 wt % of 80/20 (molar ratio) Ph-TEOS/TEOS copolymers submitted to different hydrolysis methods: (a) without treatment and treated with (b) TMBS, (c) HCl at 110°C, and (d) HCl at 60°C.

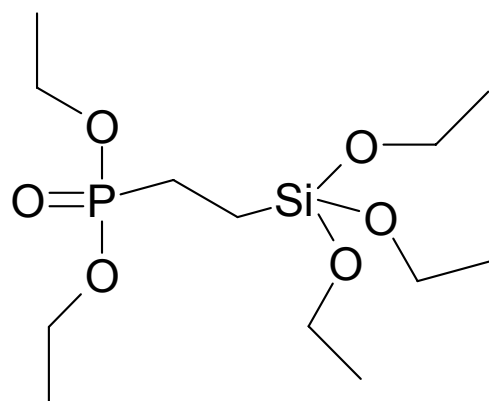
Figure 12. Histograms from the line profiles correlating the size of the periodic structures with their occurrences along a diagonal line in the AFM micrographs of composite membranes with different compositions.

Figure 13. Proton conductivity at 100% RH as a function of temperature for (1) ● plain Nafion 117® (without treatment); (2) ■ plain SPEEK (without treatment); (3) SPEEK membranes with 20 wt % 80/20 (molar ratio) Ph-TEOS/TEOS copolymer after different treatments: ▲ treated with 37% HCl at 110°C, ▼ treated with TMBS, and ◇ treated with 37% HCl at 60°C.

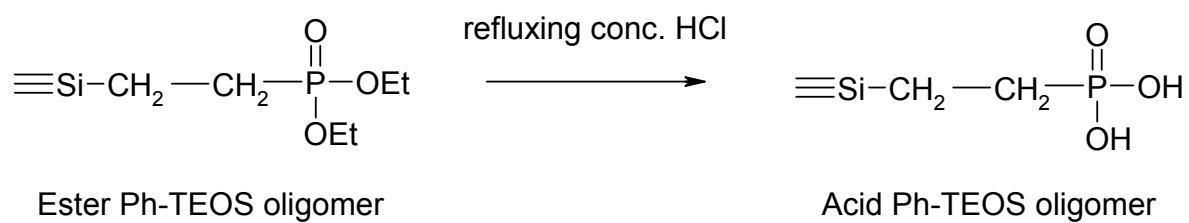
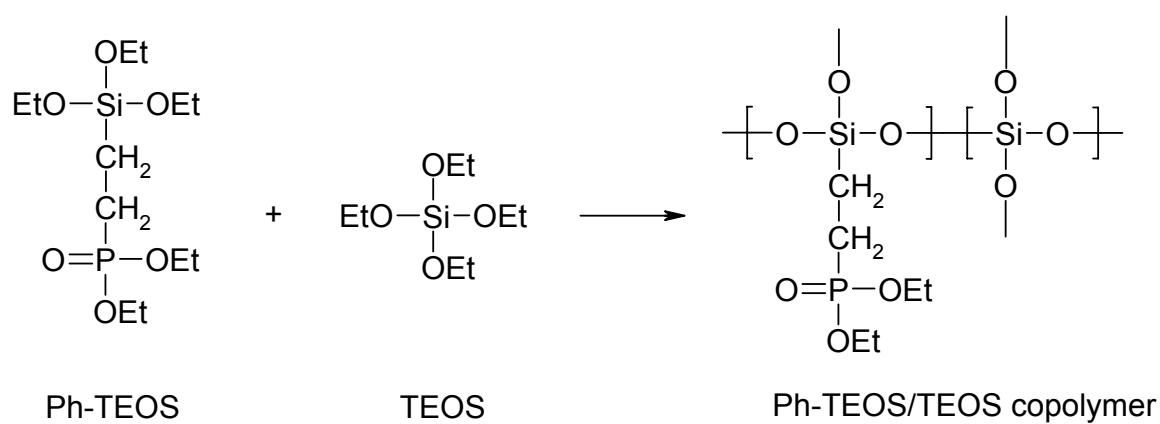
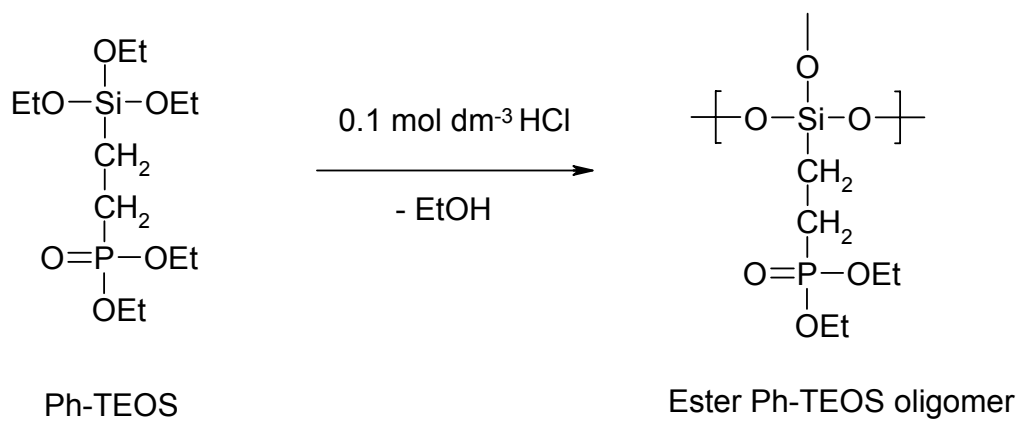
Figure 14. Proton conductivity at 100% RH as a function of temperature for different concentrations of 80/20 (molar ratio) Ph-TEOS/TEOS copolymer in SPEEK, after membrane treatment in HCl at 110°C: ■ 0 wt%, ● 5 wt%, ▲ 10 wt%, ▼ 20 wt %.

Figure 15. Proton conductivity at 100% RH as a function of temperature for different concentrations of 80/20 (molar ratio) Ph-TEOS/TEOS copolymer in SPEEK, after membrane treatment in HCl at 60°C: ▼ 0 wt%, ▲ 10 wt%, ● 20 wt%, ■ 40 wt %.

Figure 16. Proton conductivity at 80°C as function of % RH: ■ SPEEK membranes with 20 wt % (■) 80/20 or (▲) 60/40 (molar ratio) Ph-TEOS/TEOS copolymer and ● Nafion 117®. SPEEK composite membranes were treated with HCl at 60°C and washed one week in water before measuring; Nafion 117 was measured without previous treatment.



Scheme 1



Scheme 2

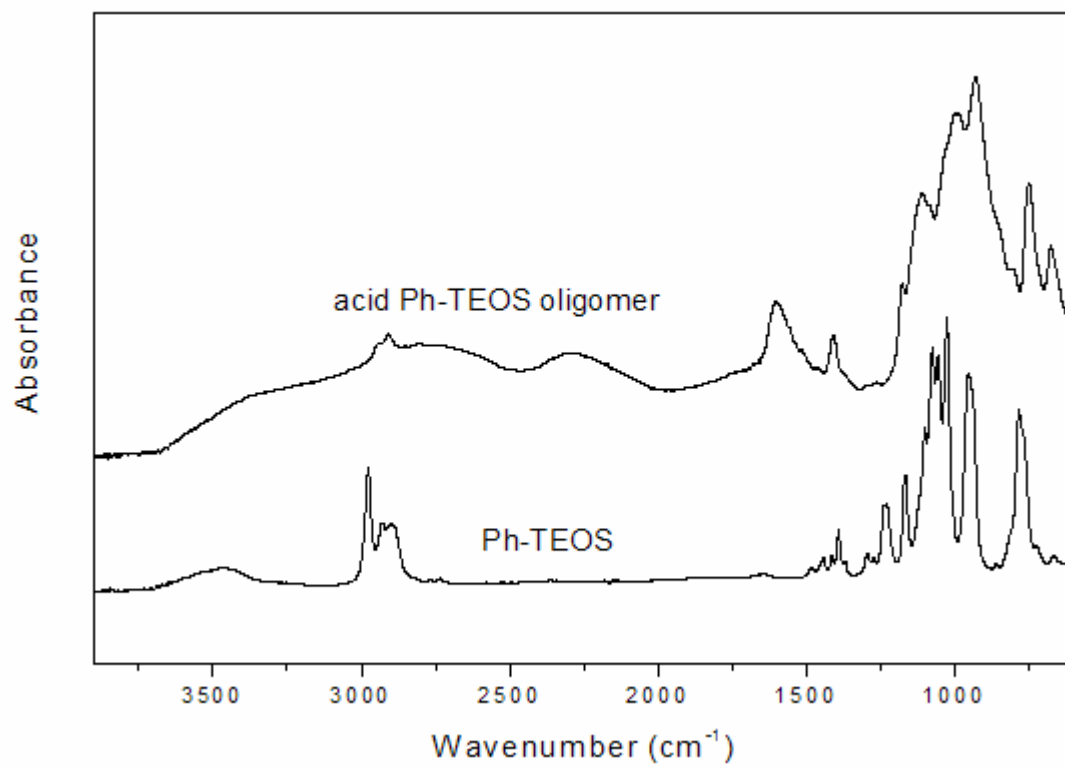


Figure 1

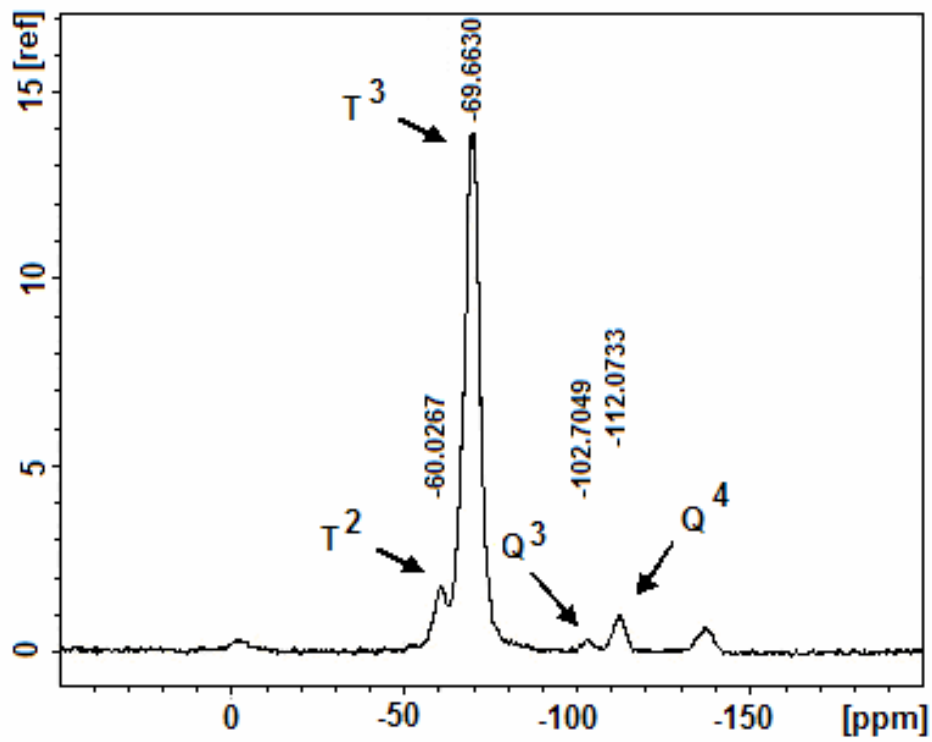


Figure 2

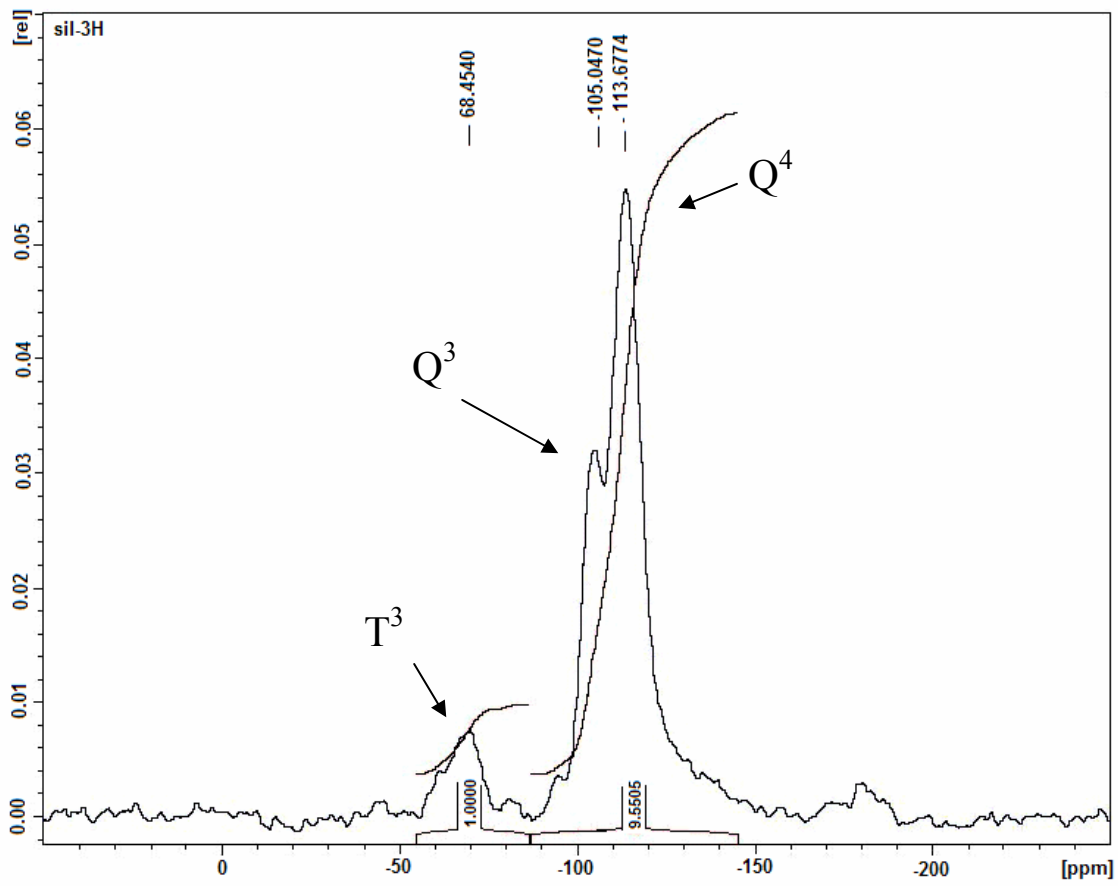


Figure 3

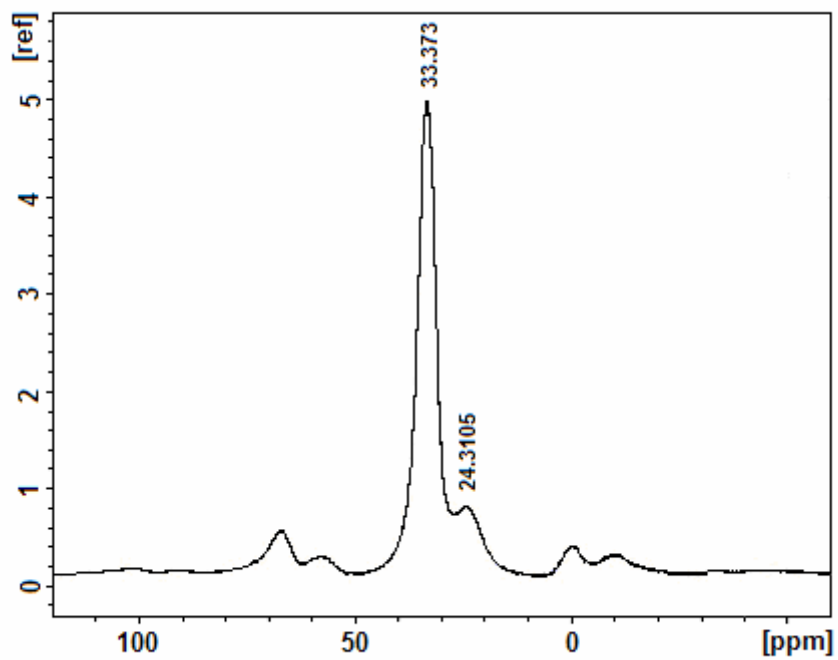


Figure 4

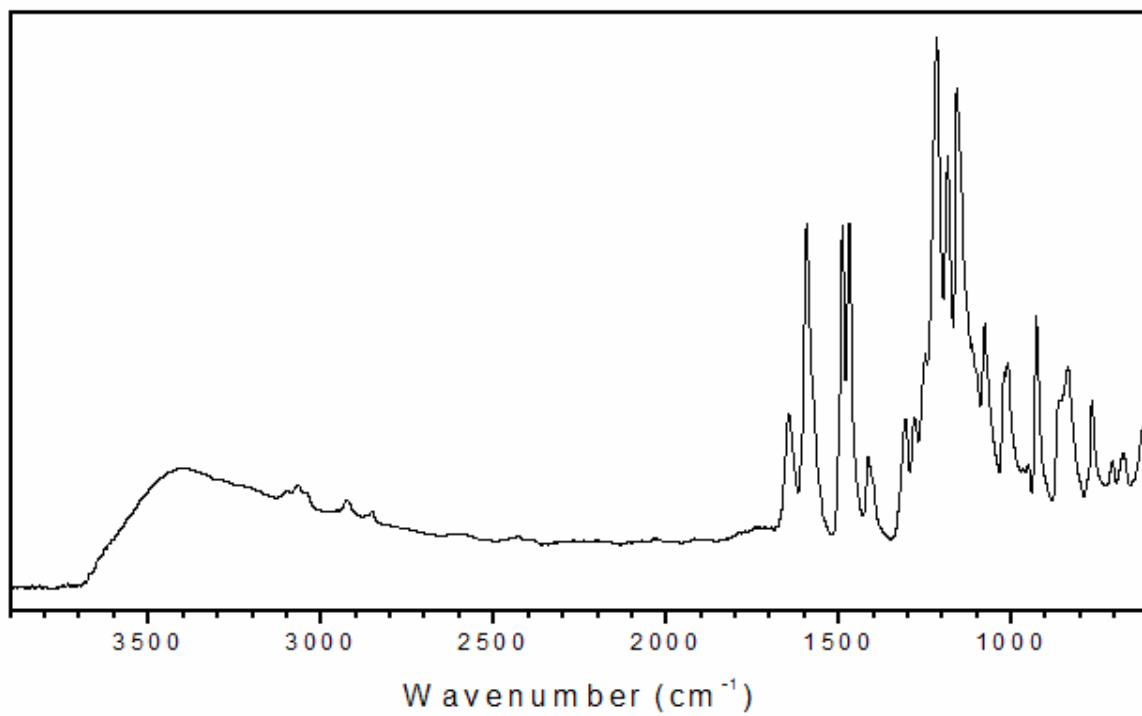


Figure 5

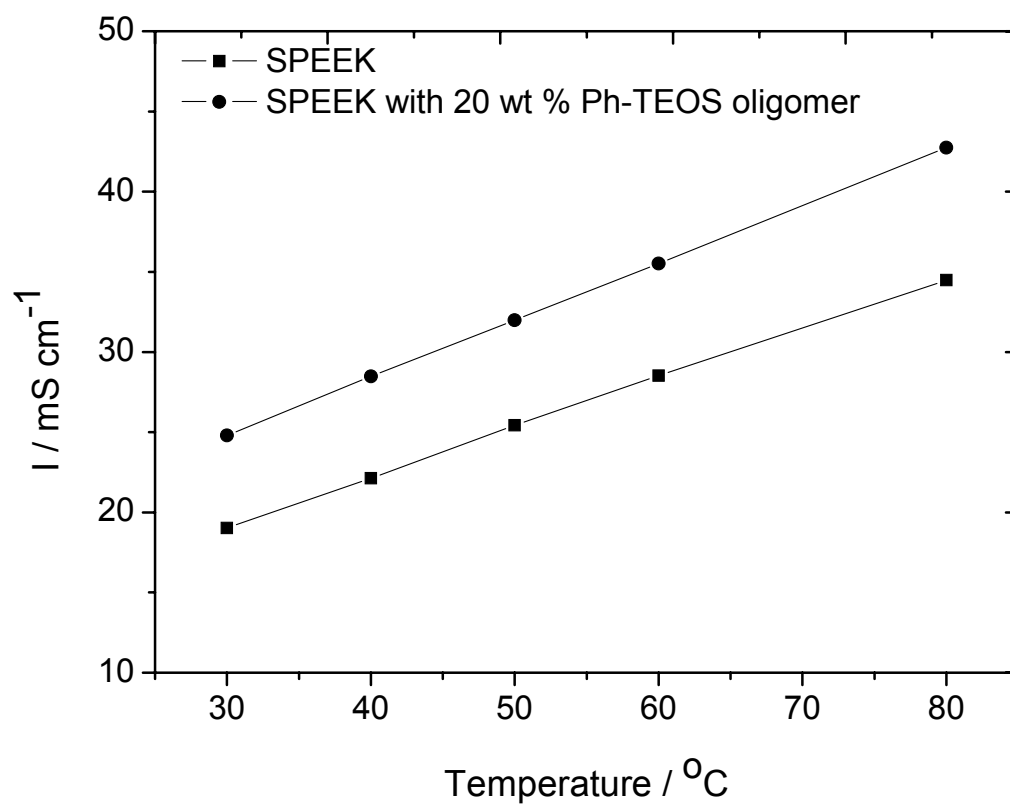


Figure 6

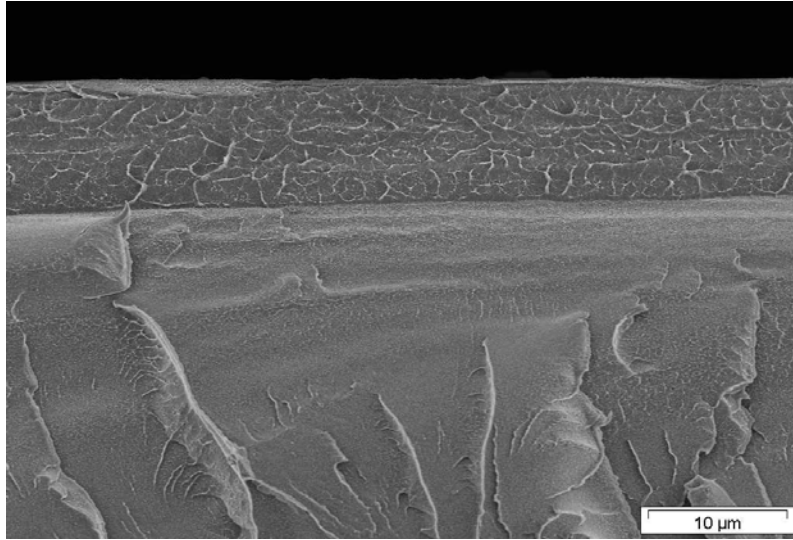


Figure 7

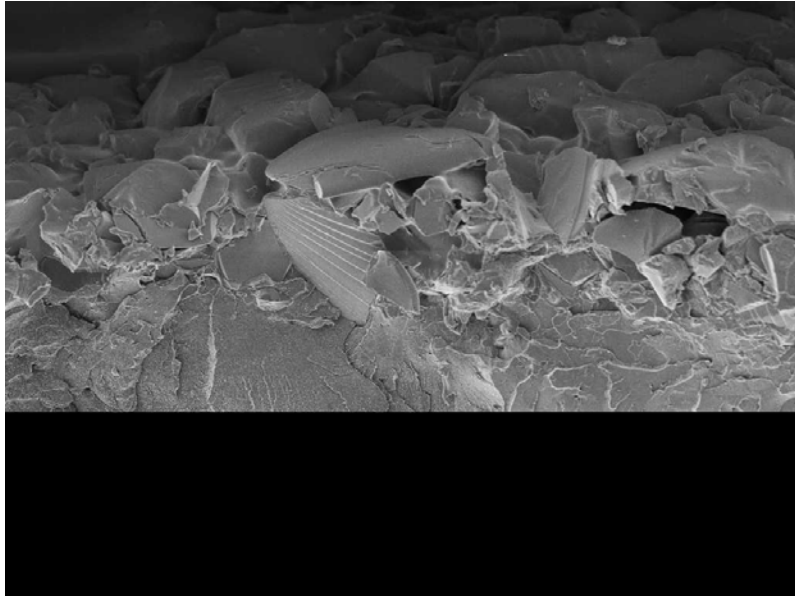


Figure 8

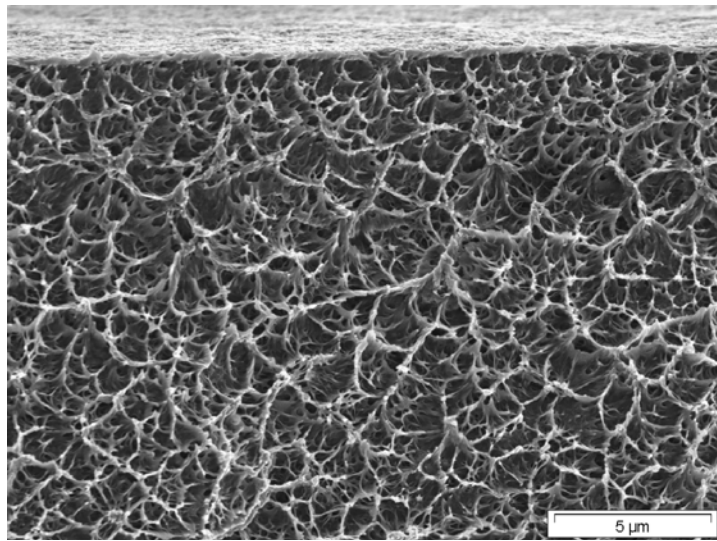


Figure 9

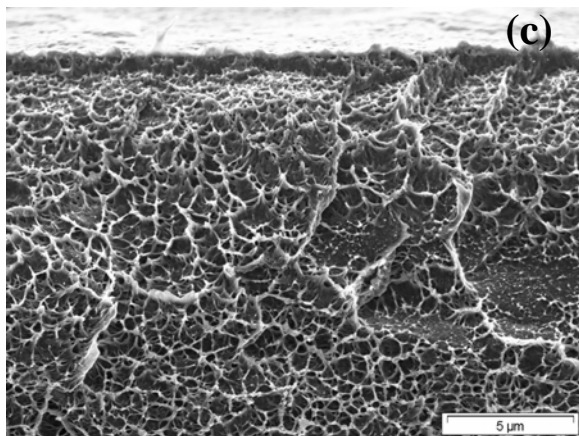
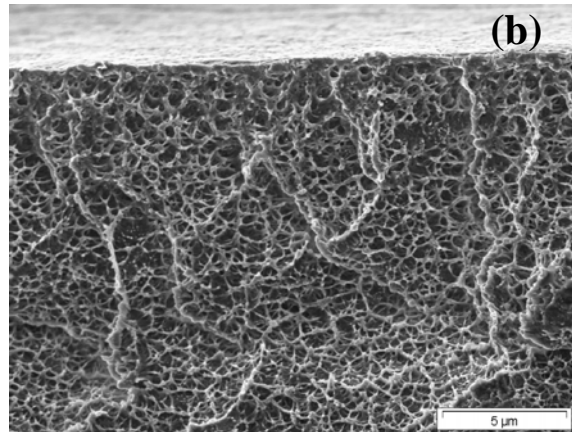
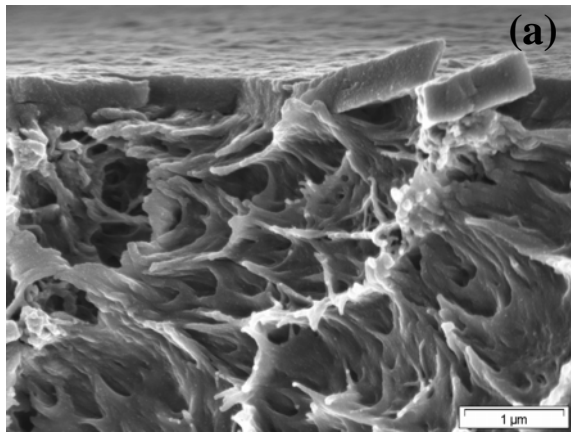


Figure 10

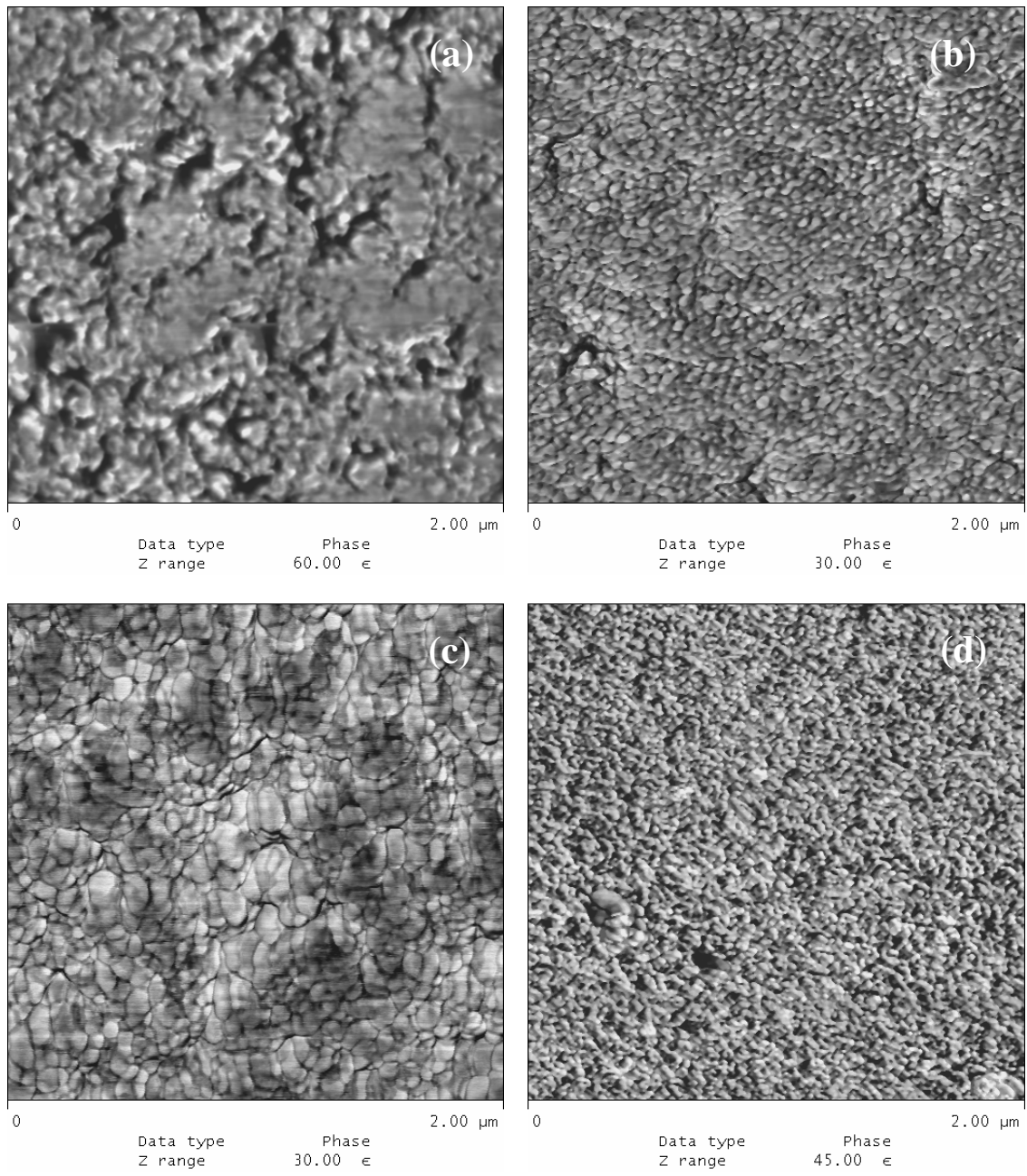


Figure 11

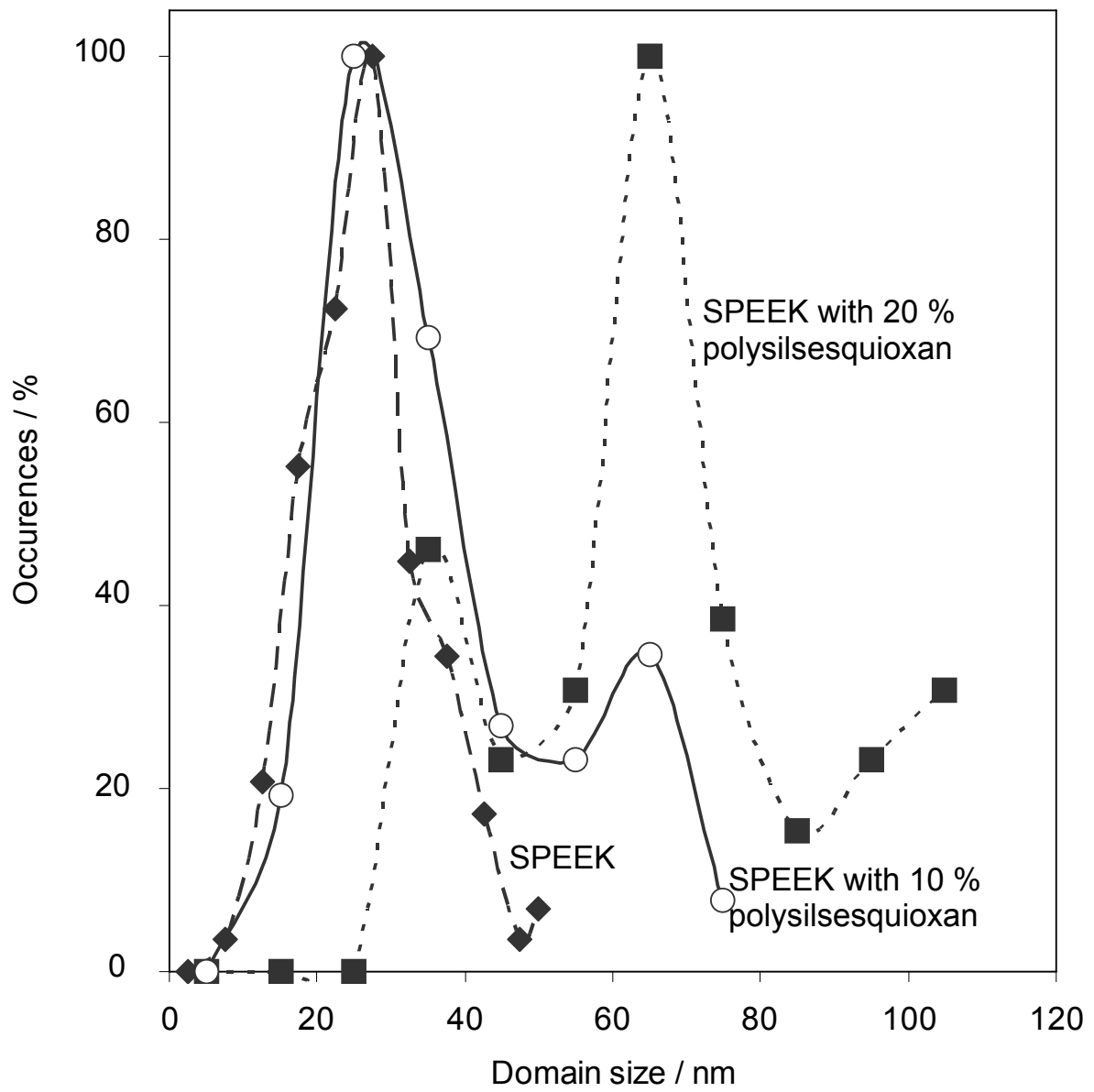


Figure 12

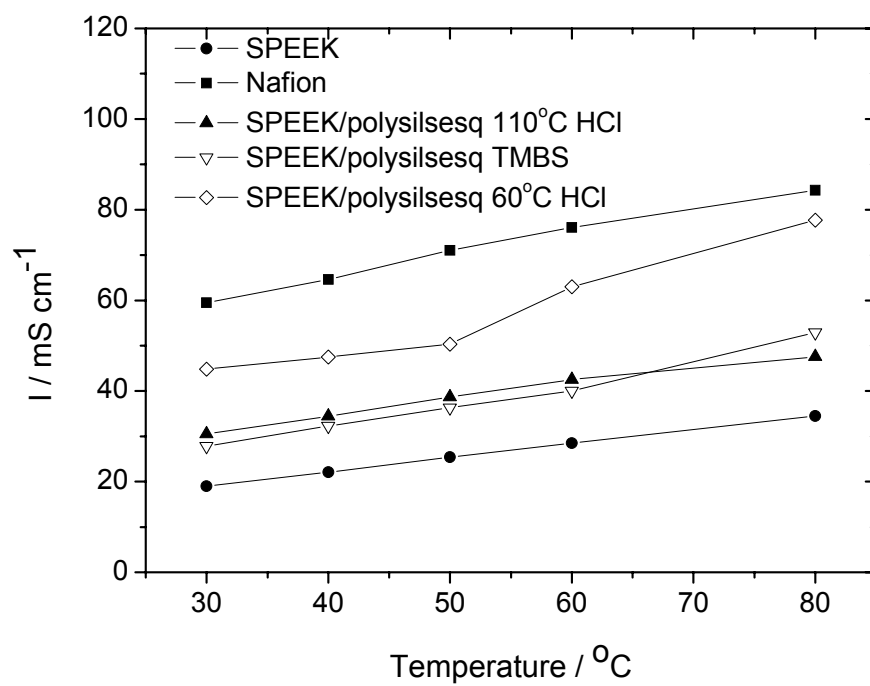


Figure 13

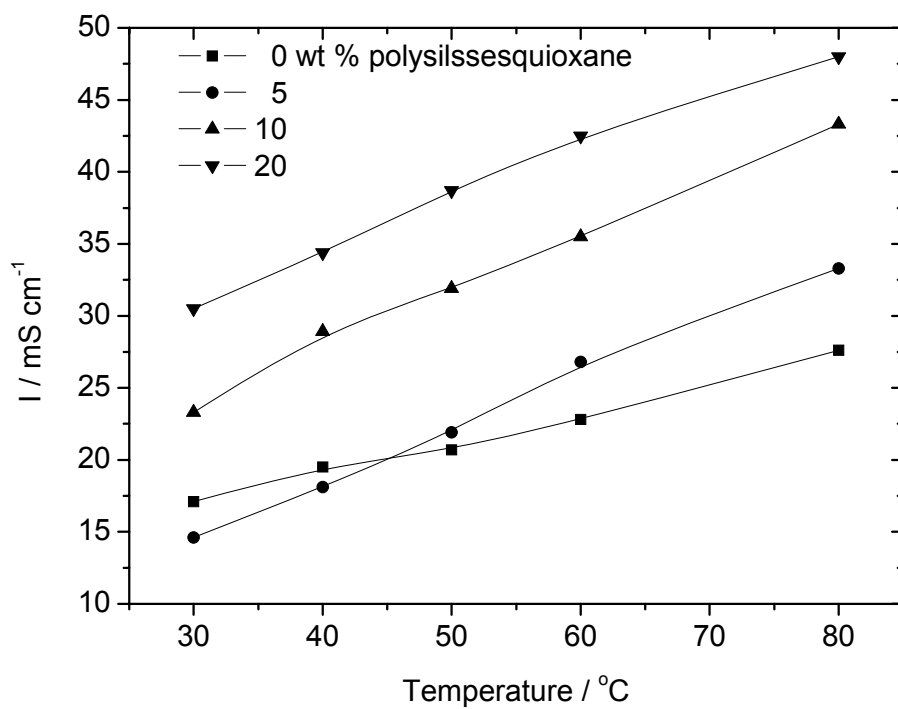


Figure 14

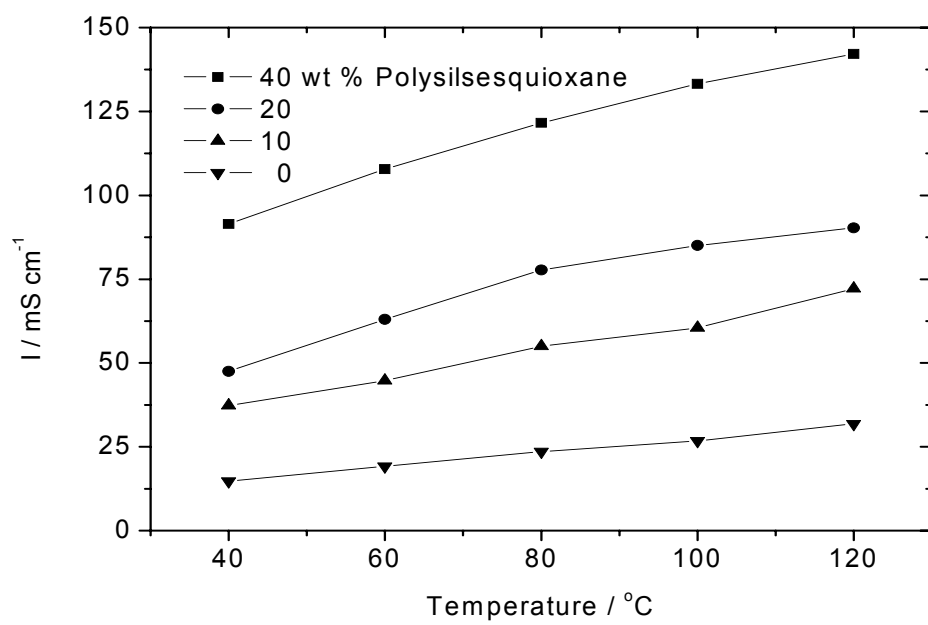


Figure 15

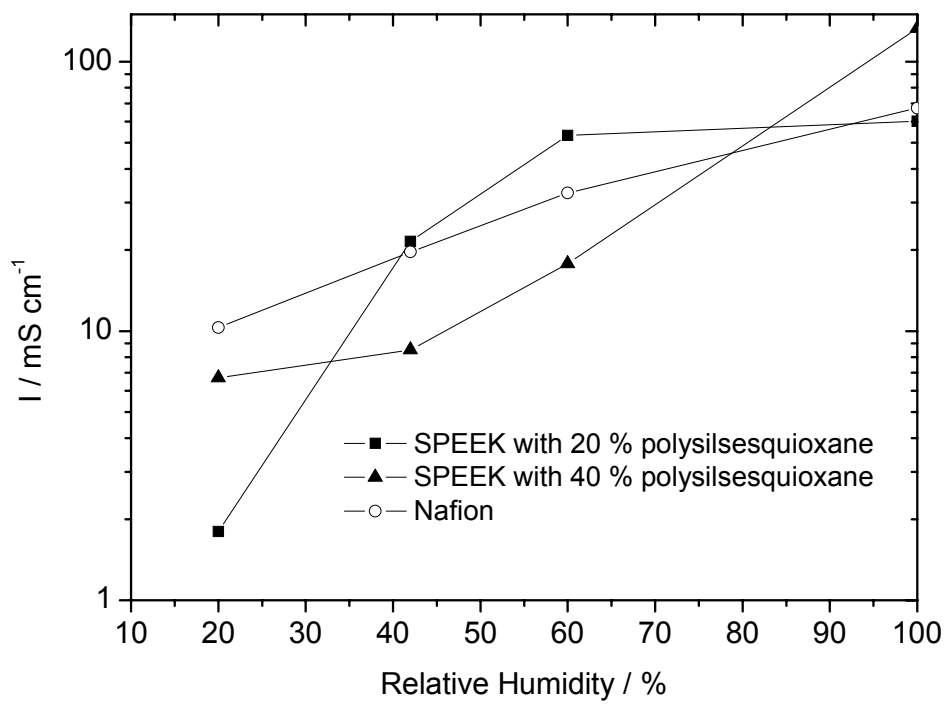


Figure 16