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Proton conducting composite membranes from polyether ether ketone and heteropolyacids for fuel cell applications

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Abstract

A series of composite membranes based on sulfonated polyether ether ketone with embedded powdered heteropolycompounds was prepared and their electrochemical and thermal properties were studied. An increase in degree of sulfonation as well as introduction of these fillers resulted in increased T_g and enhanced membrane hydrophilicity, bringing about a substantial gain in proton conductivity. The conductivity of the composite membranes exceeded 10^{-2} S/cm at room temperature and reached values of about 10^{-1} S/cm above 100°C . © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Composite membranes; Electrochemistry; Ion-exchange membrane; Polyether ether ketone (PEEK); Heteropolyacids

1. Introduction

Stimulated by the need for pollution control, the development of polymer electrolyte membrane fuel cells (PEMFC) has attracted increasing interest, particularly for automotive and stationary power applications [1–3]. Currently the solid polymer electrolyte materials used in PEMFC are either perfluorinated polymers, designated as Nafion (Du Pont) or Nafion-like polymers [4] supplied by Dow, Asahi and some other companies. The trifluorostyrene membranes (BAM3G), recently developed by Ballard [5], have also demonstrated good performances and long term stability. However, the high cost of perfluorinated polymers limits the large scale commercialization of

PEMFC. The necessity to reduce the cost of PEM is stimulating a large body of research, which aims at rationalizing the remarkably efficient combination of properties of the perfluorinated ionomers (PFI) and at developing new polymers with similar properties by a less expensive chemistry. A comprehensive review of the extensive literature on the emerging relevant materials was recently published by Savadogo [6].

It is well known [7] that such properties of PFI polymers as high hydrolytic stability and good proton conductivity are related to the hydrophobicity of the fluorinated polymer backbone and the hydrophilicity of the sulfonic acid side chain groups. The hydration of the PFI membrane is crucial for the performance of PEMFC since proton conductivity decreases drastically with dehydration. For instance, with Nafion, which loses water above 80°C the conductivity drops to very low values above this temperature. One more limitation associated with Nafion type PFI membranes

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[2,4] is the methanol cross-over when used in the direct methanol fuel cell (DMFC). This results in a decreased fuel cell performance due to depolarization of the oxygen reducing cathode. A further drawback of the perfluorinated polymers is that they are not environmentally friendly which will be important when mass-produced.

The disadvantages of PFI membranes stimulated many efforts to synthesize PEM based on partially fluorinated and fluorine free hydrocarbon ionomer membranes as alternatives to Nafion. Among them membranes based on aromatic polyether ether ketone (PEEK) were shown to be very promising for fuel cell application [6–9], since they possess good mechanical properties, thermal stability, toughness and some conductivity, depending on degree of sulfonation (DS). The approach, adopted in order to improve proton conductivity, in the present work consists of synthesizing composite membranes by incorporation of solid heteropolyacids (HPA) into partially sulfonated PEEK polymer matrices.

The chemical structure of PEEK is shown in Fig. 1. It is a thermostable polymer with an aromatic, non-fluorinated backbone, in which 1,4-disubstituted phenyl groups are separated by ether (–O–) and carbonyl (–CO–) linkages. PEEK can be functionalized by sulfonation and the DS can be controlled by reaction time and temperature. The second component of these composite membranes, HPAs, are known as the most conductive solids among the inorganic solid electrolytes at near-ambient temperature [4,10–12]. For instance, hydrated tungstophosphoric acid exhibits a room temperature conductivity of 1.9×10^{-1} S/cm [11], and its sodium form has a conductivity of about 10^{-2} S/cm [12]. The HPAs are soluble in polar solvents, where they produce stable Keggin type anions such as $\text{PW}_{12}\text{O}_{40}^{3-}$. The strong acidity of HPAs is attributed to the large size of the polyanion yielding low delocalized charge density.

When appropriately embedded in a hydrophilic polymer matrix, the hydrated HPAs are expected to endow the composite membrane with their high

Fig. 1. Effect of sulfonation time on ion exchange capacity (IEC) of PEEK.

proton conductivity, while retaining the desirable mechanical properties of the polymer film. The fillers used in the present study, were tungstophosphoric acid (TPA), its sodium salt (Na-TPA) and molybdophosphoric acid (MPA). The binder matrix was partially sulfonated PEEK (SPEEK). The sulfonated form of PEEK was used in order to provide the polymer matrix with some hydrophilicity. This paper reports the electrical and thermal properties of this new composite HPA/SPEEK membranes as a potential alternative to perfluorinated membranes in PEMFC.

2. Experimental section

2.1. Preparation of polymers

PEEK was obtained from Polysciences, Inc, USA in the form of extrudates. It was dried in a vacuum oven at 100°C overnight. Thereafter, 20 g of polymer was dissolved in 1 l of concentrated (95–98%) sulfuric acid (H_2SO_4) and vigorously stirred at room temperature for the desired time ranging from 24 to 112 h. Then the polymer solution was gradually precipitated into a large excess of ice-cold water under continuous mechanical agitation. The agitation was continued 1 h further and then the polymer suspension was left to settle overnight. The polymer precipitate was filtered and washed several times with distilled water until the pH was neutral. The polymer was then dried under vacuum for 8–10 h at 100°C. The final product is the sulfonic acid form of PEEK (SPEEK). The ion-exchange capacity (IEC) of sulfonated PEEK polymers was determined by titration: 2–5 g of the SPEEK was placed in 1 M aqueous NaOH and kept for 1 day. The solution was then back titrated with 1 M HCl using phenolphthalein as an indicator.

2.2. Heteropolycompounds

The solid HPAs were obtained from Fluka Chemicals, and were used as received. The HPAs used were tungstophosphoric acid, $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$ (TPA), molybdophosphoric acid, $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$ (MPA) and the disodium salt of tungstophosphoric acid, $\text{Na}_2\text{HPW}_{12}\text{O}_{40}$ (Na-TPA).

2.3. Differential scanning calorimetry

DSC measurements were carried out using a DuPont 910 Differential Scanning Calorimeter at a heating rate of 10°C/min under nitrogen atmosphere. Indium was used as the calibration standard. Approximately 10–15 mg samples were first dried by heating at 20°C/min to 200°C, quenched in liquid nitrogen and reheated to 250°C at 10°C/min. The glass transition temperature, T_g was calculated at the intersection of the tangents to the corresponding DSC curve.

2.4. Thermogravimetry

The TGA was carried out using a Du Pont 951 thermobalance controlled by a 2100 thermal analysis station. The approximately 15–20 mg samples were first dried at 200°C to remove any moisture/solvent for 30 min, and then programmed from 90 to 900°C at a rate of 10°C/min under a nitrogen atmosphere.

2.5. ^1H NMR

The ^1H -NMR spectra were recorded on a Varian Unity Inova spectrometer at a resonance frequency of 399.961 MHz. For each analysis, a 2–5 wt.% polymer solution was prepared in DMSO- d_6 and TMS was used as the internal standard. NMR data were acquired for 64 scans at a temperature of 30°C. The acquisition parameters were set to a spectral window of 6000 Hz (15 ppm), a pulse angle of 55°, acquisition time of 2 s and relaxation delay of 1 s. The DS was determined by integration of distinct aromatic signals.

2.6. Preparation of the composite membranes

The SPEEK polymer was first dissolved (5–10 wt.%) in dimethylacetamide (DMAc) and the appropriate weight of powdered HPA was then added to the solution. The resulting mixture was stirred for 16–24 h. After evaporation of most of the solvent the mixture was cast onto a glass plate using a casting knife. The cast membranes were dried at room temperature overnight and then at 60°C for 4–6 h and at 80–120°C overnight. The content of HPA in the dry product was 60 wt.%.

2.7. Electron microscopy

The morphology of the composite polymer membranes was investigated using a scanning electron microscope (JSM-849, JEOL). Fresh cross-sectional cryogenic fractures of the membranes were vacuum sputtered with a thin layer of Au/Pd prior to SEM examination.

2.8. Water absorption of membranes

The amount of water absorbed in sulfonated PEEK membranes was determined in two ways. The freshly prepared dry SPEEK membranes were weighed and immersed in H₂O at room temperature until no more weight gain was observed. Wetted membranes were blotted dry with absorbant paper before weighing again. In another experiment the wet membranes were vacuum dried at 100–120°C and their water loss determined, then they were soaked again in water and weighed after blotting. The vacuum dried membranes when immersed in water for hydration regained the initial weight of the wet membranes within 4–6 h. The weight gain of absorbed water was calculated with reference to the weight of the dry specimen: $(W_{\text{wet}}/W_{\text{dry}} - 1) \times 100\%$.

2.9. Conductivity measurements

The proton conductivity of the polymer membrane samples was measured by the AC impedance spectroscopy technique over a frequency range of 1–10⁷ Hz with oscillating voltage 50–500 mV, using a system based on a Solartron 1260 gain phase analyzer. A sample of the membrane with diameter 13 mm was placed in an open, temperature controlled cell, where it was clamped between two blocking stainless steel electrodes with a permanent pressure of about 3 kg/cm². The main shortcoming of an open cell is specimen dehydration during the measurement. It is compensated by advantages such as the possibility of providing good electrode-specimen contact (by applying sufficient thrust using an external load) and access to a larger temperature range (typically up to 150°C). Special weightings have shown that the specimen discs (100–500 µm) soaked in water prior to the test and tightly compressed between blocking electrodes, lose

on the average 5% of water during the heating up to 50°C, about 25% of water up to 100°C and about 65% of water when heated up to 140°C over the time scale of the experiment. This obviously impairs the determination of the true proton conductivity, which however, can be only underestimated due to partial dehydration of the specimens in these measurements. Therefore, the results of the conductivity tests can be regarded as an evaluation of a lower limit of the membrane conductivity at a given temperature.

The conductivity σ of the samples in the transverse direction was calculated from the impedance data, using the relation $\sigma = d/RS$ where d and S are the thickness and face area of the sample, respectively, and R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Re(Z) axis. The impedance data were corrected for the contribution from the empty and short-circuited cell.

3. Results and discussion

3.1. Sulfonation of PEEK

Sulfonation of PEEK was carried out using (95–98%) H₂SO₄ which avoids degradation and cross-linking reactions [13,14] which occur at sulfonation with 100% H₂SO₄ or with chlorosulfonic acid sulfonation agents. Cross-linking presumably involves sulfone groups, the concentration of which is negligible when H₂SO₄ contains a few percent of water, because H₂O decomposes the aryl pyrosulfate intermediate, required for sulfone formation [13].

The PEEK was sulfonated for different reaction times ranging from 24 to 112 h to produce polymers of various DS. It is known that the DS can be controlled by changing reaction time, acid concentration and temperature, which can provide a sulfonation range of 30–100% per repeat unit [12,13]. It has been observed in [13] that PEEK dissolved in H₂SO₄ does not undergo molecular weight degradation even over long periods of time.

It is worth noting that SPEEK is heterogeneous with respect to the DS of individual repeat units. This is important to consider, as it might influence SPEEK properties, such as crystallinity and solubility [13,15]. The heterogeneity is aggravated by the slow kinetic of

dissolution of PEEK in sulfuric acid, which depends on the molecular weight of the polymer chains and their accessibility (surface of granules dissolves before the bulk). The solubility of PEEK in strong acids can be attributed to protonation of the ketone groups and in some cases to chemical modification (e.g. sulfonation) of the polymer [14,15]. Sulfonation is an electrophilic reaction and its effectiveness depends on the substituents present on the aromatic ring. In PEEK, the hydroquinone unit (between the ether bridges) can be sulfonated under relatively mild conditions, being doubly activated towards electrophilic reactions.

The physical and chemical properties of SPEEK depend on the concentration of sulfonic groups and the nature of counter ions. Sulfonation modifies the chemical character of PEEK, reduces the crystallinity and, consequently affects solubility. Thus, at DS lower than 30% SPEEK is soluble only in strong H_2SO_4 . Above 30% DS the SPEEK polymers are soluble in hot dimethylformamide (DMF), dimethylacetamide (DMAc) and dimethylsulfoxide (DMSO); above 40% they are soluble in the same solvents at room temperature; above 70% they are soluble in methanol and at 100% sulfonation in hot water [13,14].

The ion-exchange capacity (IEC) of SPEEK polymers measured at room temperature is presented in Fig. 1 as a function of sulfonation reaction time. It can be seen that IEC increases continuously with reaction time. Upon sulfonation, PEEK reached an IEC close to 2.0 meq/g within 112 h.

3.2. Determination of the degree of sulfonation

The degree of sulfonation was determined quantitatively by ^1H NMR using a variation of the method described in [16] for SPEEK polymers. In the ^1H NMR spectra, the presence of a sulfonic acid group causes a significant 0.25 ppm down-field shift of the hydrogen H_E compared with H_C , H_D in the hydroquinone ring. The nomenclature of the aromatic protons for the SPEEK repeat unit is given below: Scheme 1.

The presence of each SO_3H group results in a distinct signal for protons at the E position. The intensity of this H_E signal, yields estimates of the H_E content which is equivalent to the SO_3H group content. The ^1H NMR signal for the SO_3H group is less easy to record directly because this proton is labile. The ratio between the peak area of the distinct H_E signal (A_{H_E}),

Scheme 1. Nomenclature of the aromatic protons for the SPEEK repeat unit.

and the integrated peak area of the signals corresponding to all the other aromatic hydrogens ($A_{\text{H}_{\text{A},\text{A}',\text{B},\text{B}',\text{C},\text{D}}}$), is expressed as

$$\frac{n}{(12 - 2n)} = \frac{A_{\text{H}_\text{E}}}{\sum A_{\text{H}_{\text{A},\text{A}',\text{B},\text{B}',\text{C},\text{D}}}} \quad (0 \leq n \leq 1)$$

where n is the number of H_E per repeat unit. An estimate of the degree of sulfonation x is obtained as: $x = n \times 100\%$.

The ^1H NMR spectra of different SPEEK samples dissolved in DMSO- d_6 are shown in Fig. 2. Since non-sulfonated PEEK is insoluble in any solvent except in strong acids, its ^1H NMR spectrum could not be recorded. However, in the low sulfonated SPEEK, a significant proportion of repeat units are non-sulfonated and the H_C and H_D of the unsubstituted hydroquinone ring of PEEK repeat units in the SPEEK polymer appear as a characteristic singlet at 7.25 ppm. The intensity of this singlet decreases as the DS increases. Simultaneously two new signals increasing in intensity with higher DS are associated with the hydroquinone ring of the SPEEK repeat unit. H_C is a doublet of doublets at 7.20 ppm and the two $\text{H}_{\text{B}'}$ protons are a doublet at 7.00 ppm, shifted upfield by the proximity of the SO_3H group. The multiplicity of H_C doublet of doublets is caused by four bond coupling with H_E (2.5 Hz) and its three bond coupling with H_D (8.8 Hz). The intensities of both H_C and the two $\text{H}_{\text{B}'}$ increase proportionally with the intensity of H_E .

The DS calculated from the ^1H NMR spectra of SPEEK samples is plotted in Fig. 3. These data are also reported in Table 1 together with the sulfur content calculated from DS and with results of elemental analysis for sulfur. The sulfur percentage determined experimentally compared with the one, calculated from the estimated values of DS, are in reasonably good agreement. The ion exchange capacity (IEC) and the sulfur

Fig. 2. ^1H NMR spectra of sulfonated PEEK samples.

Fig. 3. Sulfur content in SPEEK as function of degree of sulfonation, DS.

content, given in Fig. 4, also agree rather well with each other. Thus, the sulfonation at room temperature during 24–112 h yields ionomers of PEEK with DS ranging from 40 to 80 mol% (0.4–0.8 sulfonic groups per repeat unit).

3.3. Glass transition temperature: DSC studies

The values of the glass transition temperature T_g were determined by the DSC technique at a heating rate of 10°C/min. From Fig. 5 it can be seen that T_g increases monotonically with the DS. The introduction of $-\text{SO}_3\text{H}$ groups into the PEEK polymer increased the T_g by as much as 65°C for the sample having a DS of 80% relative to T_g of 150°C for non-sulfonated PEEK. These results agree with those obtained in reference [15] for PEEK. Similar behavior has also been

observed for sulfonated polysulfone [17–20]. The increase in T_g with the degree of sulfonation results from the increased intermolecular interaction by hydrogen bonding of SO_3H groups (ionomer effect). Increased molecular bulkiness may also contribute [19]. It is likely that these intermolecular forces hinder the internal rotations compared to unsulfonated PEEK. Interestingly similar conclusions have been reached from the observations that sulfonation increases the molecular dimensions of PEEK in solution [13].

3.4. Thermal stability: TGA studies

The thermal stability of sulfonated and pure PEEK was investigated by TGA. The samples were pre-treated at 200°C and then the experiment was run from 90 to 900°C at a heating rate of 10°C/min under

Table 1
Sulfur content of different sulfonated SPEEK samples

Sample	Degree of sulfonation (DS) by NMR (mol%)	Sulfur content (wt.%)	
		Experimental (elemental analysis)	Calculated from DS
PEEK	0.0	0.0	0.0
SP1	48	3.90	4.3
SP2	51	4.45	4.63
SP3	56	5.15	5.06
SP4	68	6.60	6.08
SP5	72	7.0	6.4

Fig. 4. Comparison of IEC and sulfur content as functions of DS of SPEEK.

Fig. 5. T_g of SPEEK as a function of DS.

flowing nitrogen. Examples of TGA and DTG curves of PEEK and SPEEK are shown in Fig. 6. Since PEEK is a temperature resistant polymer, the onset of weight loss for this polymer, obviously due to the main chain decomposition, starts at about 520°C. The pyrolytic degradation of PEEK results in the formation of phenols and benzene. The major pyrolysis product of PEEK is phenol, which is produced in the early chain scission reaction involving ether rather than carbonyl linkages [21].

In Fig. 6 two weight loss steps are observed for SPEEK, which is reflected by two broad peaks in the DTG curve in two separate temperature ranges. The first weight loss peak in SPEEK is believed to be due to the splitting-off of sulfonic acid groups. A similar observation was made for sulfonated polysulfones [18,19]. The maximum of the second peak for all SPEEK samples shifted to 560° from 600°C for PEEK. The maximum corresponding to the sulfonic acid decomposition, was found to be at 360°C in the TGA/DTG for all the sulfonated samples. From the first peak the weight loss corresponding to the sulfonic acid decomposition was determined (Table 2) and plotted against DS, as shown in Fig. 7. The theoretical weight loss calculated assuming that the splitting-off of a sulfonic acid group releases one SO_3 molecule, is given in Fig. 7. As can be seen, there is a rather close

Fig. 6. TGA and DTG curves of PEEK and SPEEK.

agreement between the weight loss calculated theoretically and the one determined from TGA experiments for the sulfonic acid decomposition. This indicates that desulfonation is the first event in the thermal degradation process.

The onset temperature of SPEEK pyrolysis, given in Fig. 8, indicates that SPEEK membranes are thermally stable up to approximately 300°C and that this temperature is only marginally affected by an increase in the degree of sulfonation up to 80%. It should be noted that

Table 2

Measured and calculated weight loss of different SPEEK samples due to the splitting-off of sulfonic acid groups

Sample	Degree of sulfonation by NMR, mol%	Weight loss by TGA, wt. %	Weight loss calculated, wt. %
SN1	40	13.0	10.0
SP2	51	15.0	12.2
SN2	65	16.5	15.3
SN3*	70	17	16.4
SN4*	74	19.5	17.0
SN5	76	19.0	17.4
SN6*	80	20.0	18.2

* Polymers, used for preparation of the composite HPA/SPEEK membranes.

the thermal stability observed under non-equilibrium conditions of TGA experiment might be overestimated to some extent. However, the thermal analysis results evidenced that the thermal stability of the SPEEK membranes is quite sufficient and that SPEEK will be stable enough within conceivable temperature range of PEMFC application.

3.5. Water absorption of SPEEK membranes

The main purpose of sulfonating aromatic PEEK is to enhance acidity and hydrophilicity as it is known that the presence of water facilitates proton transfer

and increases the conductivity of solid electrolytes. The enhancement of hydrophilicity by sulfonation of PEEK polymer can be followed by water absorption of SPEEK membranes as a function of the degree of sulfonation. In Fig. 9 the water uptake of SPEEK membranes is plotted against the number of sulfonic acid groups. The water uptake increased with DS and reached 120 wt.% for a SPEEK membrane with 80% DS (0.8 SO₃H groups per repeat unit). These results show that the water absorption of SPEEK membranes increased linearly up to a DS of 65% and thereafter very rapidly above 70%. In the highly sulfonated SPEEK the density of SO₃H groups is high which

Fig. 7. Weight loss by TGA due to sulfonic acid decomposition.

Fig. 8. Onset temperature of SPEEK decomposition.

Fig. 9. Water absorption by the SPEEK membranes.

may involve clustering or agglomeration. Clustered ionomers absorb more water, therefore, a large water uptake may be suggestive of the presence of ion-rich regions [14] where proton transfer is particularly fast.

A similar trend was observed for the water content of Ballard's BAM3G membranes [5,6], which showed an increase in swelling when equivalent weight (EW) decreased from 920 to 375, where the EW is expressed as (gram of polymer)/(mol-SO₃). The water uptake in BAM3G membranes increased exponentially below 410 EW to more than 250%. This is similar to our results where the water content increased linearly with an increase in sulfonic group density up to a DS of ca. 65% and then increased exponentially. The water content of our SPEEK membranes is higher than in Nafion117 (34%), Dow membranes (56%), NASTA membranes (48%) [6] and polyimide membranes (30%) [22]. The high water adsorption capacity of SPEEK membranes compared to others is also a characteristic of BAM3G membranes.

3.6. Scanning electron microscopy

The morphology of the composite SPEEK/HPA membranes has been studied by scanning electron microscopy. A typical example of SEM micrograph of the cryogenic fracture of a composite membrane is presented in Fig. 10. It can be seen that the solid HPA is well mixed with SPEEK and shows no ag-

Fig. 10. SEM micrograph of the cryogenic fracture of the composite membrane SPEEK-70/TPA.

glomeration after membrane preparation. From this micrograph the HPA particles are observed to be of size 0.05–0.15 µm and homogeneously distributed within the SPEEK membrane.

3.7. Conductivity studies

Prior to conductivity measurements all the membrane samples were soaked in water for hydration. The effect of the DS on the conductivity of SPEEK membranes at room temperature is shown in Fig. 11. The conductivity was found to increase with DS and reached a value of 8×10^{-3} S/cm for 80% DS. With increasing DS there is an enhancement in the solubility of SPEEK in organic solvents (e.g. DMAc) and the crystallinity decreases as previously reported in [13]. As a consequence, the polymer becomes more hydrophilic and absorbs more water, which facilitates proton transport. Hence, the sulfonation raises the conductivity of the PEEK not only by increasing the number of protonated sites (SO₃H), but also through formation of water mediated pathways for protons. Proton conductivity also depends on factors such as density and distribution of sulfonic acid sites and degree of dissociation of sulfonic acid functions.

The influence of temperature on the conductivity for a series of SPEEK membranes at different DS is presented in Fig. 12. As can be seen, the membrane with 40% DS did not show any improvement in conductivity with temperature; on the contrary the conductivity even decreased with increase in temperature. The conductivity of the 48% sulfonated membrane increased up to 85°C and then dropped sharply to very low values. Membranes sulfonated at 70 and 74% showed a continuous increase in conductivity and a gradual decrease beginning only above 100°C. Finally the conductivity of the 80% sulfonated membrane behaved differently compared with the others. The conductivity increased slowly in the range of 20–50°C, more rapidly between 50 and 100°C and then gradually increased again up to 145°C.

The temperature dependence of SPEEK conductivity suggests the presence of two competing trends, one of which enhances and the other reduces conductivity. As ionic conductivity of electrolytes is in general thermally stimulated, it is natural to expect a rise in proton conductivity with temperature. The decay in the conductivity curves above a certain tem-

Fig. 11. Conductivity of SPEEK membranes at ambient conditions.

perature, which is observed (Fig. 12) for all but one of the SPEEK samples, suggests that dehydration of the polymers occurs during the measurements. This dehydration apparently starts at room temperature for 40% SPEEK, and then shifts towards higher temperatures as the DS increases. Thus, it is not only the capacity of water uptake which is important (Fig. 9), but also the capacity of the membrane to retain water. For instance, the sample with 40% DS loses water so fast that dehydration suppresses any conductivity rise. With increasing DS the conductivity curves show less steep declines, and for 80% SPEEK water retention is so high that dehydration induces only a decrease in the rate of increase of conductivity up to 145°C. Since the low sulfonated membranes were not found to maintain high conductivity at temperatures higher than 90°C, the SPEEK polymers sulfonated at 70–80% were selected as the matrix for the preparation of composite membranes with heteropolyacids.

Composite SPEEK/HPA membranes were prepared by incorporation of 60 wt.% HPA (TPA, MPA and Na-TPA) into three SPEEK matrices with 70, 74 and 80% degree of sulfonation. The thickness of these composite membranes varied from 150 to 300 μm (Table 3). The conductivity of the composite membranes was measured at temperatures ranging from 20 to

150°C. The results, showing the effects of solid HPA incorporation and temperature on the conductivity of these composite membranes, are given in Figs. 13–15. They are presented for three different sets of composite membranes, containing the various solid HPA into each of the three SPEEK matrices. Incorporation of HPAs increased the membrane conductivity compared to the pure membrane, except in the case of the 80% sulfonated PEEK for which only the TPA/SPEEK membrane showed enhanced conductivity at temperatures higher than 80°C. In all cases, the introduction of the HPAs improves the high temperature stability of the conductivity. The conductivity of all the composite membranes behaved in a similar fashion: the TPA based membranes showed a higher conductivity than Na-TPA and MPA composites. It appears that TPA, being a stronger acid, systematically yields a higher proton conductivity increase as well as a better water retention at high temperature. These results evidence that it is possible to increase significantly the proton conductivity of SPEEK matrices by incorporation of solid HPAs.

The water uptake at room temperature and the conductivity of some of these membranes along with their thickness are given in Table 3. The water uptake of the composite membranes increased upon incorporation

Fig. 12. Conductivity of SPEEK membranes with different DS as a function of temperature.

Table 3

Conductivity and water absorption of the composite membranes

Membrane designation	Membrane type	Thickness of wet membrane, μm	Water-uptake, wt. %	Conductivity, S/cm	
				25°C	100°C
SN3	Pure SPEEK 70	300	48	1.3×10^{-3}	6.7×10^{-3}
HPA1	SPEEK 70+ TPA	170	64	3.5×10^{-3}	1.7×10^{-2}
HPA2	SPEEK 70+ Na-PA	375	143	2.9×10^{-3}	1.5×10^{-2}
HPA3	SPEEK70+MPA	200	94	3.1×10^{-3}	1.1×10^{-2}
SN4	Pure SPEEK 74	300	62	2.1×10^{-3}	9.5×10^{-3}
HPA4	SPEEK74+ TPA	160	190	5.1×10^{-3}	2×10^{-2}
HPA5	SPEEK74+NaTPA	300	160	4.5×10^{-3}	1.6×10^{-2}
HPA6	SPEEK 74 + MPA	200	146	3.6×10^{-3}	1.2×10^{-2}
SN6	Pure SPEEK 80	500	120	8.0×10^{-3}	7.6×10^{-2}
HPA7	SPEEK80+TPA	300	600	2×10^{-2}	9.5×10^{-2}
HPA8	SPEEK80+NaTPA	200	400	1.4×10^{-2}	5.8×10^{-2}
HPA9	SPEEK 80 + MPA	160	320	1.2×10^{-2}	3.0×10^{-2}

Fig. 13. Effect of different HPAs on the conductivity of composite membranes as a function of temperature, 70% DS.

Fig. 14. Effect of different HPAs on the conductivity of composite membranes as a function of temperature, 74% DS.

of hydrophilic solid HPA into SPEEK matrices. It can be noted that the pure 80% DS SPEEK membrane shows higher conductivity above 100 °C than its composite membrane containing MPA or Na-TPA (Fig. 15). The pure 80% DS SPEEK membrane has a

thickness of 500 μm which is three times higher than the MPA composite membrane (160 μm) and more than twice the thickness (200 μm) of the Na-TPA containing membrane. The moisture retention can be affected by the thickness of the membranes. Obviously,

Fig. 15. Effect of different HPAs on the conductivity of composite membranes as a function of temperature, 80% DS.

the thicker membranes will have lower dehydration rate upon heating, than the thinner membranes. At the same time the positive effect of HPA introduction can be clearly seen at temperatures below 60°C for MPA and below 80°C for Na-TPA.

Comparing these results with similar studies by Park et al. [23] for sulfonated polysulfone membranes containing solid TPA, where the conductivity of 1.6×10^{-3} S/cm was registered, the proton conductivity displayed by HPA-SPEEK membranes proved to be much higher. In a work of Tazi and Savadogo [24] a conductivity of 9×10^{-2} S/cm was reported for H_2SO_4 acidified Nafion-silicotungstic based membranes having thickness of 200–300 μm . Despite the fact that we used only fluorine-free polymeric materials, the membranes reported in this work exhibited conductivities of the same order of magnitude.

4. General discussion

From the results of water absorption it can be noted that the water content of the SPEEK membranes increases with DS. At the same time T_g also increases, reflecting an increased intermolecular association

through the polar ionic sites. The increasing association of the PEEK repeat unit with the anionic counter charge ($-\text{SO}_3^-$) immobilized on the polymer backbone of a neighboring chain suggests a less effective separation of the aqueous phase compared to Nafion. This increased association is not however, sufficient to upset the effect of the increased water content, which brings about an increase in conductivity of SPEEK membranes. The proton conductivity in aromatic membranes depends much more on the amount of water as second phase than in the case of Nafion [25]. The higher water content of these membranes helps the migration of proton, which involves such species as H_3O^+ and H_2O_5^+ , needed for high conductivity.

The composite membranes containing HPAs display higher T_g s than the pure SPEEK membranes. For example, the membranes containing TPA and MPA in 70% DS SPEEK showed a T_g increase from 208 to 215°C. This increase in T_g of the composite membranes may be due to a reduction in chain mobility most probably caused by the interaction of the solid acid with polar groups of the SPEEK polymer chain [17]. Such interaction is also consistent with the SEM micrographs of the composite membranes, which show fine particles of HPA uniformly distributed

within SPEEK polymer (Fig. 10). This uniformity in distribution is favorable for proton transport as it minimizes interparticle distances.

The composite membranes absorb more water than the pure SPEEK membranes. The water content (Table 3) of the membranes based on SPEEK with 70% DS increases from 48 to 143%, for membranes with 74% DS it increases from 62 to 190%, and for membranes based on 80% DS SPEEK it increased from 120 to the high value of 600%. It is worth noting however, that the increased water uptake associated with the incorporation of HPAs to the polymer matrix is only one of the factors affecting the membrane conductivity. The other factors, including the polymer intrinsic conductivity, strength, density and softness of the solid acid sites, the solid phase loading, particle size and spatial distribution, the aqueous phase dispersion, all affect the dependence of conductivity on the water content. In the case of Nafion membranes which are described as nanoporous inert ‘sponges’ for water of hydration, this water shows little interaction with the polymer chain and forms hydration shells around the sulfonic acid groups [26]. In HPA/SPEEK composite membranes, the aqueous phase is more continuous. This leads to higher water uptake (swelling) and contributes to a greater extent to proton conductivity.

Examples of Arrhenius plots of conductivity for the 70% SPEEK based composite membranes are given in Fig. 16. For all composite membranes reported here,

Fig. 16. Arrhenius plots of conductivity for composite membranes with 70% DS.

the activation energy for proton conduction was similar and close to 15 kJ/mol. This result suggests a common charge transfer mechanism. The relatively low measured values of activation energy are suggestive of a liquid like mechanism most probably based on the Grotthus reorientational proton transfer scheme [4].

It is important to mention that the conductivity of composite membranes was not affected by storage in water at room temperature for 9 months. SPEEK polymer therefore, acts as an effective polymer matrix for solid HPA. The results of this study have indeed shown that composite membranes containing solid HPA are stable for the long term, with no change in their conductivity. These composite membranes possess good mechanical strength and flexibility except for those based on 80% sulfonated SPEEK which become weak because of excessive swelling. The best mechanical properties were found for the 70% DS SPEEK based composites.

5. Conclusions

In this study a series of composite membranes have been prepared by incorporation of tungstophosphoric acid, its disodium salt or molybdophosphoric acid into partially sulfonated PEEK polymer. These membranes exhibited a rather high conductivity of 10^{-2} S/cm at ambient temperature and up to a maximum of about 10^{-1} S/cm above 100°C . The DSC studies of these membranes for the glass transition temperature showed an increase in its value due to the incorporation of both sulfonic acid groups and the solid HPA into the PEEK polymer. The increase in T_g of the composite membranes compared with the T_g of pure SPEEK suggests an intermolecular interaction between SPEEK and HPAs. These membranes are thermally stable up to temperatures above 250°C , as well as being mechanically strong and flexible. They maintain the high conductivity during storage in water for several months. These composite membranes are easy to prepare and much less expensive than the commercial perfluorinated membranes. Their high proton conductivity combined with their long-term stability qualify the HPA/SPEEK composite membranes to be considered for use in PEM fuel cells as alternatives to Nafion based membranes.

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