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Nanocomposite Membranes Based on Sulfonated Poly(etheretherketone) Structured with Modified Silica for Direct Ethanol Fuel Cell

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Summary: Polymer blend of sulfonated poly(oxy-1,4phenyleneoxy-1,4phenylenecarbonyl-1,4phenylene) (SPEEK) and poly(ether sulfone) (PES) was compounded with commercial and synthesized silica. PES phase had important role to improve the stability and to reduce permeability of sulfonated matrix to alcohol solution, but it also reduced the proton conductivity of membrane. The addition of synthesized silica, which had heteropolyacid phosphotungstic acid (HPW) occluded inside the silica matrix ($SiO_2 \cdot HPW$) was evaluated to improve the conductivity.

Keywords: alcohol; barrier; composite; ethanol; fuel cell; membrane; pervaporation; phosphotungstic acid; poly(ethersulfone) (PES); polymer blend; proton conductivity; silica; sulfonated poly(aryletheretherketone) (SPEEK)

1. Introduction

Diverse segments of society and governments are engaged in making feasible the fuel cell technology as an alternative power sources to replace actual engines fed by petroleum fractions. The fuel cell that uses polymer electrolyte fuel cell (PEFC) presents attractive operational conditions, such as low working temperature range (10–120 °C) and absence of corrosive and harmful fluids as electrolytic medium. Because of these aspects, PEFC is the most suited energy generator for portable devices and vehicle. Actually, there are two main types of PEFC, fed by hydrogen or alcohol. This study focuses the development of membranes for direct ethanol fuel cell (DEFC), in order to replace commercial perfluorinated membranes. Ethanol has been used as an attractive alternative to the fossil fuel, because it is a renewal fuel source, besides it has higher energy density than hydrogen, handy to transport, easy to manipulate and nearly safe. All these aspects ensure logistic and cost advantages for ethanol compared to hydrogen in fuel cell program, especially for domestic application and light vehicles.

The development of proton conducting membranes based on sulfonated polymers to provide mobile proton sources for use in alcohol medium presents additional challenger than that in hydrogen medium, due to the affinity of alcohol to the sulfonic groups. To overcome drawbacks such as instability and high alcohol permeability of membranes, polymer blend membranes consisting of sulfonated (a) and unsulfonated (b) polymers have been proposed for direct methanol fuel cell.[1,2] The main role of unsulfonated polymer is to reduce the access of alcohol to sulfonic groups of sulfonated polymer, so the membrane becomes more resistant to alcohol. Besides mechanical stability and good properties of barrier, the membrane should present other

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features such as relative permselectivity to water-alcohol, mechanical and oxidative resistance and good level of protonic conductivity.

Heteropolyacids (HPA) have been used as additive in compositions of sulfonated polymers to enhance its proton conductivity. However, HPA used to come out from membrane, when it is immersed in hot water,[3,4] making the additive useless. To manage this drawback, one immobilizes phosphotungstic acid (HPW) inside the silica matrix.

2. Experimental

2.1. Materials

Poly(oxy-1,4phenyleneoxy-1,4phenylene-carbonyl-1,4phenylene) (PEEK) ($M_n = 10{,}300$, $M_w = 20{,}800$, $T_m = 322\,°C$), tetraethyl orthosilicate (TEOS) 98% of purity and phosphotungstic acid hydrate $H_3PW_{12}O_{40} \cdot xH_2O$ (HPW) mp = 95 °C were purchased from Aldrich; sulphuric acid conc.95-98%wt, n-buthyl alcohol, ethyl alcohol absolute and 96°GL and 1-methyl-2-pyrrolidone (NMP) were purchased from Vetec; poly(ethersulfone) (PES) Ultrason® E120 and silica Tixosil®333 were kindly supplied by BASF and Rhodia respectively.

2.2. Sulfonation of Polymer

The procedure of sulfonation was based in literature.[5] Dried PEEK was dissolved in sulfuric acid under mechanical stirring and nitrogen atmosphere. The reaction mixture was stirred and maintained at 23 °C. The time of reaction varied in according to the desired sulfonation degree. Past the reaction time, the polymer solution was poured into a large excess of cold water under vigorous stirring, to precipitate the polymer. After washing with water the sulfonated polymer was dried in vacuum oven.

The determination of ion exchange capacity (IEC) and sulfonation degree was done by titration method using solution of NaOH 0,1N and phenolphthalein as indicator. The following expressions were used to determine the IEC (1) and the sulfonation degree (2).

$$IEC = \frac{n^\circ meq_{SO_3H}}{weight_{SPEEK}} \tag{1}$$

where *IEC, n°meq* are ion exchange capacity (meq/g) and miliequivalents number respectively. The unit of weight is expressed in grams.

$$SD = \frac{MW_p \times IEC}{1000 - (80 \times IEC)} \times 100 \tag{2}$$

where *SD, MW_p*, are sulfonation degree (%) and molecular weight of mero unit of polymer.

2.3. Synthesis of Silica with HPW Occluded

The synthesis of $SiO_2 \cdot HPW$ was based on Izumi's[6] work. The sol-gel process employed the acid-catalised condensation reaction. Aqueous solution of 1-butanol (0.25 mol) and HPW (6×10^{-4} mol) in water (2.5 mol) was prepared. After TEOS (0.25 mol) addition the solution was stirred mechanically and heated at 60 °C for 6 hours. The hydrogel obtained was dried and purified by extraction in water at 80 °C for 3 hours. After drying at 70 °C under vacuum, the silica was grounded and sifted in sieve of 270 mesh.

2.4. Preparation of Composite

Polymer blend were prepared mixing pre-filtered solutions of SPEEK (IEC = 1.874 meq/g) and PES in 1-methyl 2-pirrolidone at proportion of 5:5 in mass. Suspensions of silica in SPEEK/PES were sonicated with a high intensity ultrasonic probe for 40 min.

Characterization of silicas were analysed on FTIR spectrometer Nicolet model Magna IR-760 on KBr pellets and on Rigaku Miniflex diffractometer by X-ray diffraction (XRD) technich, which operates with $CuK\alpha_1$ irradiation. Contents of phosphorus, tungsten and silicon were estimated by X-ray fluorescence Bruker-axs Explorer model S-4. The specific surface area of $SiO_2 \cdot HPW$ particle was measured by using BET method with nitrogen adsorption at

77°K in an accelerated surface area and porosity system Micromeritics ASAP 2010. Particle size and shape of silica and morphology of fractured membranes were observed by scanning electron microscope (SEM) JEOL JSM 5610LV. Impedance measurements of membranes were performed on Autolab PGSTAT-30 at range of 10 Hz–1 MHz and amplitude of 10 mV, using stainless steel electrodes on samples pre-treated in deionized water at 60 °C for 1 hour.

3. Results and Discussion

Amorphous silica of Tixosil® 333 and HPW are taken as reference. Infrared spectra are shown in Fig. 1. The infrared pattern of silica showed stretching vibration bands of O–H and Si–O at 3470 and 1100 $\mathrm{cm^{-1}}$ respectively. The pure HPW presented three bands of vibration at 1079 $\mathrm{cm^{-1}}$, it corresponds P=O stretching band; the terminal oxygen band W=O at 978 $\mathrm{cm^{-1}}$ and the bridging oxygen bands W–O–W at 887 and 797 $\mathrm{cm^{-1}}$. These characteristics bands are in agreement with literature.[7] The silica particle synthesized with HPW ($SiO_2 \cdot HPW$) presented bands at 3480 ν(O–H) and 1090 $\mathrm{cm^{-1}}$ ν(Si–O). Specific interactions are observed by small displacements of bands seen at 1090, 951, 901 (shoulder) and 804 $\mathrm{cm^{-1}}$. In addition, this spectrum is quite similar to spectrum of $SiO_2 \cdot HPW$ particles, containing 5% of HPW, which was characterized by Kukovecz.[8]

The content of HPW in silica particle was 8.3% in wt, estimated by X-ray fluorescence.

XRD patterns of silicas analysed in powder were compared in Fig. 2. Basal reflections of $SiO_2 \cdot HPW$ were found dislocated from amorphous SiO_2 pattern (composed mainly by cristobalite, it is localized at 21.9°) [9] to higher angles next to signals corresponding to pure HPW ($H_3PW_{12}O_{40} \cdot 6H_2O$) reported by Ponzi [10] at $2\theta = 10.7°$ and 26.6°. All physical methods applied confirmed the formation of silica matrix by sol-gel process and the presence of HPW crystal in $SiO_2 \cdot HPW$ particles.

According to Kim [11], the BET surface area of pure HPW was 5.0 m^2/g, and in case of silica containing HPW immobilized, $SiO_2 \cdot HPW$ was 216 m^2/g and it was comparable to 292 m^2/g obtained in this study for bulk particles smaller than 0.053 mm. The average pore diameter of 20 A° and the curve shape classified it as microporous particles.

The SEM micrographs are displayed in Fig. 3. The starting particle size of bulk

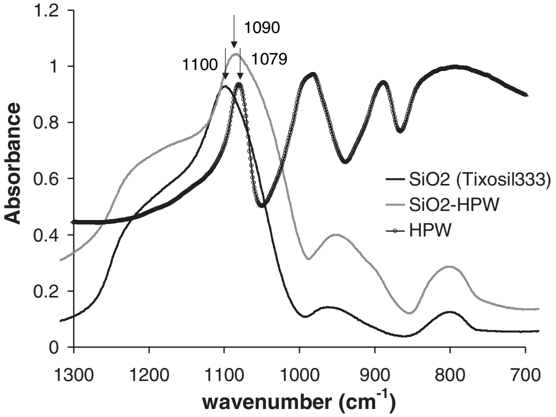


Figure 1.
Infrared spectra of silicas SiO_2 (—) and $SiO_2 \cdot HPW$ (—) and HPW only (-o-).

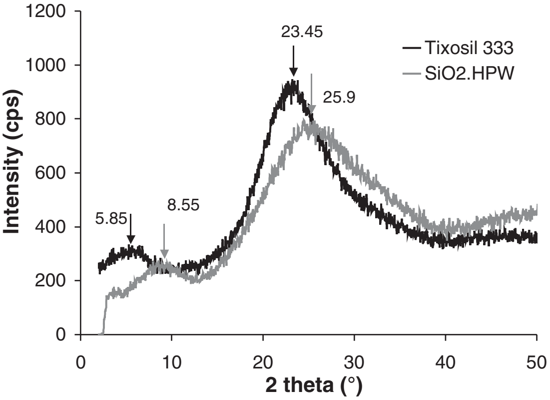


Figure 2.
XRD patterns of silica.

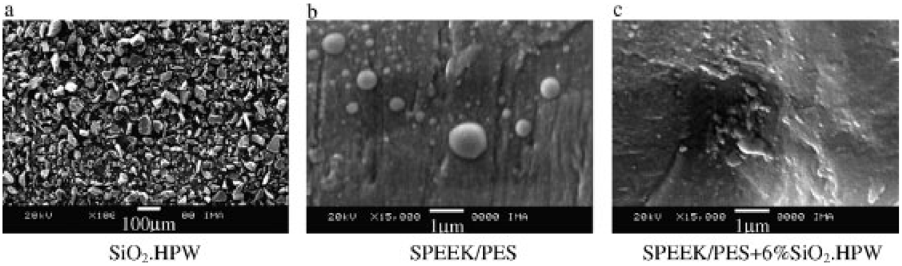
powder of $SiO_2 \cdot HPW$ was smaller than 100 μm (a). The morphology of polymer blend SPEEK/PES prepared by magnetic stirring resulted in rougher heterogeneous phase (b), compared to the composite of $SiO_2 \cdot HPW$ particles sonicated in solution of polymer blend. The last process reduced the inorganic particles to nanoscale and the heterogeneous polymer phase was not more observed by this technique (c).

Stability of membranes was evaluated in ethanol-water solution 4.0 M, which going through 40 up to 90 °C, then membranes were weighted at preset times during 24 hours for each temperature. Ethanol solution uptakes on membranes were shown in Fig. 4.

All polymer membranes resisted temperatures until 90 °C, except pure SPEEK, that did not resist even at 40 °C (not represented). The addition of $SiO_2 \cdot HPW$ slightly reduced the swelling in membranes. The type of silica seems to affect differently the mechanical property. The membranes prepared with $SiO_2 \cdot HPWHPW$ became tougher, while the other one compounded with Thixosil® 333 (precipitated amorphous silica) presented segregation and the membrane became brittle.

The pervaporation test was carried on at two different concentrations of ethanol solution 1.5 M and 4.0 M and the temperature was kept at 55 °C. The data are presented in Table 1.

Results showed that permeated flux increased with concentration of ethanol solution, as it was expected. In addition, all composite membranes based on polymer blend had better results than Nafion®. Although the addition of silica particles



SiO₂.HPW SPEEK/PES SPEEK/PES+6%SiO₂.HPW

Figure 3.
Micrographs: (a) $SiO_2 \cdot HPW$ particle, (b) and (c) composite membranes.

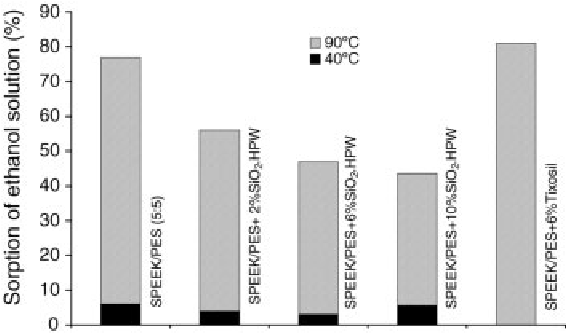


Figure 4.
Ethanol solution uptake in composites of SPEEK/PES (5:5).

Table 1.
Permeated flux of ethanol solution through membranes at 55 °C.

Membranes	Permeated and normalized flux to 100 μm thickness (kg/m^2 · h)	
	Ethanol sol. [1.5 M]	Ethanol sol. [4.0 M]
Nafion®117	3.96	4.79
SPEEK/PES (5:5)	0.20	0.39
SPEEK/PES + 2%SiO$_2$ · HPW	nr	2.34
SPEEK/PES + 6%SiO$_2$ · HPW	0.14	0.23
SPEEK/PES + 10%SiO$_2$ · HPW	0.92	nr
SPEEK/PES + 6%SiO$_2$ (Tixosil)	nr	0.60

nr – not realized.

augmented slightly the permeated flux, the amount of ethanol solution was still low.

Protonic conductivity of membranes was carried on going through 40–90 °C at 100% RH. Little amount of HPW.SiO$_2$ (2%) was enough to enhance proton conductivity of membrane, while 6% of SiO$_2$ (Tixoxil333) impaired the conductivity as seen in Table 2.

The co-relation of temperature and conductivity is represented by Arrhenius equation shown in Fig. 5.

The activation energies of membranes SPEEK/PES and SPEEK/PES+2%HPW · SiO$_2$ were 14.2 and 13.4 kJ/mol respectively. These values were higher than Nafion®117 (10.8 kJ/mol),[12] it means that the effect of temperature on conductivity response was more significant to this polymer blend than to Nafion®. This behavior can be related to higher ionic dissociation constant of Nafion® than SPEEK based membranes, due to stronger acid character of sulfonic group attached onto perfluorinated backbone, Nafion® was less affected by temperature on acid dissociating.

Table 2.
Proton conductivity of membranes at different temperatures.

Membranes	Conductivity (mS/cm)		
	40 °C	80 °C	90 °C
SPEEK/PES (5:5)	8.4	19.5	nr
SPEEK/PES + 2% HPW-SiO$_2$	21	37	65
SPEEK/PES + 10% HPW-SiO$_2$	14	21	nr
SPEEK/PES + 6%SiO$_2$ (Tixosil)	6	9	nr

nr – not realized.

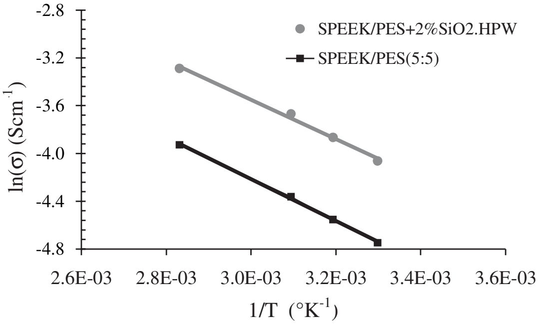


Figure 5.
Arrhenius plot of proton conductivity.

4. Conclusion

Morphology analysis showed good dispersion of both $SiO_2 \cdot HPW$ particles and polymeric phases that were reduced at nanoscale. Little amount of $SiO_2 \cdot HPW$ (2%) was enough to impart good proton conductivity. Although, the inorganic particle impaired slightly the barrier properties of membranes to ethanol solution, the amount passed through was still low. In addition, the good compatibility of $SiO_2 \cdot$ HPW particles with SPEEK/PES matrix resulted in toughened membranes, besides it contributed to reduce the membrane swelling in ethanol solution. All these features make this synthetic silica promising for imparting proton conductivity of SPEEK/PES membrane for direct ethanol fuel cell (DEFC) application.

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