Nanostructured Polyelectrolytes Based on SPEEK/TiO$_2$ for Direct Ethanol Fuel Cells (DEFCs)

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Abstract: Proton-conducting hybrid membranes consisting of poly(ether ether ketone) sulfonated (SPEEK) and titanium oxide (TiO$_2$) were prepared using the sol-gel technique for application in direct ethanol fuel cells. The effect from TiO$_2$ incorporation on membrane properties such as ethanol uptake, pervaporation and proton conductivity was investigated. The uptake and permeated flux decreased with increasing content of TiO$_2$. The ethanol permeability was about one order of magnitude smaller than Nafion® 117. FTIR spectra indicated that PEEK was sulfonated and the second degradation temperature of SPEEK58 samples confirmed the titanium oxide incorporation. The proton conductivity in ethanol solution was of the order of 10^{-3} S cm^{-1} when 4 or 8 wt% TiO$_2$ were added, and generally increased with addition of TiO$_2$.

Keywords: *Poly(ether ether ketone), sulfonation, titanium oxide, DEFCs.*

Introduction

The possible shortage of non-renewable resources associated to the reinless consumption of fossil fuels has been forcing the introduction of alternative energy conversion devices, such as fuel cells, for a variety of mobile and stationary applications[1-3]. Fuel cells are electrochemical devices able to convert chemical energy (Gibbs energy, ΔG) into electric energy spontaneously and directly by oxi-reduction reactions employing hydrogen as a fuel, generally[2-6]. Among the fuel cell types, Proton Exchange Membrane Fuel Cells (PEMFC) has been preferred due to reasons like relatively low temperature operation and large range of applications[2-4]. PEMFCs usually apply water-swollen ion-exchange polymer membranes as proton conducting electrolytes at highly water-swollen state[6-8]. In the last 20 years, direct ethanol fuel cells (DEFCs) have attracted considerable attention, as they offer several potential benefits, such as high efficiency, high power density, low or zero emission and reliability[9-13]. Ethanol is considered a liquid fuel from renewable sources (green fuel), presenting high power density (8000 W h kg^{-1}), low emission of pollutants and easy distribution and storage, taking great logistical advantage over the hydrogen[13-17]. However, one of the biggest challenges when alcohols were used in low temperature PEMFCs is high liquid fuel crossover and low proton conductivity. In order to minimize these limitations, organic-inorganic composites membranes have been widely studied for direct alcohol fuel cells (DAFCs)[18-21]. Nafion® membranes from DuPont have been used in DAFCs due to their good mechanical, thermal and chemical stability up to medium temperatures (< 90°C) and high proton conductivity in hydrated state[22]. Hybrid organic-inorganic proton-conducting membranes have been considered, since inorganic oxide presents low alcohol permeability due to an increase of membrane barrier properties[23]. In order to evaluate their potential applications for hydrogen fuel cells, the proton conductivities of sulfonated poly(ether ether ketone) (SPEEK) membranes have been studied[24,25]. Kreuer reported recently microstructure differences between SPEEK and Nafion®, demonstrating SPEEK membrane advantages over Nafion® membranes for DAFCs applications such as excellent chemical resistance, high thermo-oxidative stability and low cost[25,26]. For SPEEK polymer membranes it has been reported that the incorporation of inorganic oxides by sol-gel method leads to composite membranes with lower water and alcohol permeability and greater mechanical stability than pure SPEEK membranes for fuel cells applications[19,27,28]. We consider a similar strategy adopted by Di Vona and coworkers[19] for this work, which consists in the incorporation of titanium oxide (TiO$_2$) via *in situ* sol-gel process on the sulfonated poly(ether ether ketone) (SPEEK) polymer matrix with 58% of sulfonation degree. The main objective of this paper was to evaluate the TiO$_2$ incorporation effect on hybrid membrane properties such as ethanol uptake, pervaporation and proton conductivity in order to consider these hybrid composite membranes for direct ethanol fuel cells (DEFCs) applications.

Experimental

Materials

Poly(ether ether ketone) (PEEK) 450P, was supplied by Victrex™ USA Inc. Titanium tetrabutoxide (Ti(C$_4$H$_9$O)$_4$) or (Ti(OBu)$_4$) was supplied by MERCK-Schuchardt. 2,4-pentanedione (acetylacetone - acac) was purchased from Aldrich Chemical Co. 1-Methyl-2-pyrrolidone (NMP) 99% and sulfuric acid (H$_2$SO$_4$) 96% were supplied by VETEC Química Fina LTDA. All chemicals were used as received without further purification.

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Preparations of sulfonated PEEK (SPEEK)

PEEK was sulfonated up to a sulfonation degree (SD) of 58% according to literature[29,30]. PEEK (10g) was dried in a vacuum oven at 100 °C overnight. Then, it was added to sulfuric acid (200 mL) at room temperature. After dissolution, the reaction mixture was stirred for up to 4 h at 50 °C to achieve the desired conversion. SPEEK was precipitated in cold deionized water (below 5 °C) and washed with deionized water until the pH was close to 6. Then, the sulfonated polymer was dried under nitrogen by 12 h at 70 °C and in a vacuum oven at 80 °C for 24 h. The SPEEK degree of sulfonation (the fraction of repeat units bearing a –SO_3H group) was determined by titration: 0.3 g of SPEEK was dissolved in NMP and, at room temperature, deionized water was added. Then, the solution was titrated with 0.1 N aqueous NaOH using phenolphthalein as an indicator.

Preparation of proton-conducting hybrid membranes

The dried SPEEK was dissolved in 1-methyl-2-pirrolidone to make a 7 wt% solution under magnetic stirring at 70 °C. After that, SPEEK solution was cooled until room temperature. Then, a sol prepared adding Ti(OBu)_4 to a acac solution (1:2.2 molar ratio) in NMP (1 mL) at 0 °C was added to that SPEEK solution according to previously reported[19]. The resulting mixture was stirred at room temperature for 1 h and then, was cast onto a Petri dish and heated to dryness. The resulting membranes were peeled off and dried at 80 °C in a vacuum oven for 72 h for complete solvent removal. The amount of titanium alkoxide was calculated to produce samples containing 100:0, 98: 2, 96:4, 94:6, 92:8 90:10 and 88:12 wt% SPEEK/TiO_2 ratios. The membranes thickness was about 200 μm. All the samples were tagged as SPEEK 58 + X% TiO_2 (X=2, 4, 6, 8, 10 and 12).

Uptake measurements

The membrane uptake was determined by measuring the change in the weight before and after the hydration. The water uptake was performed in deionized water and the ethanol uptake was determined in ethanol solution 20 wt% in deionized water, separately. Weight of dry membrane (W_{dry}) was determined after completely drying in vacuum oven at 40 °C for 48 h or immediately after heat treatment at the end of the proton-conducting membranes preparation. The membrane was soaked in water and ethanol solution for 24 h, and then surface-attached humidity onto membrane was removed with filter paper. After that, the wetted membrane weight (W_{wet}) was determined as quickly as possible. The uptake was calculated by using the following Equation 1:

$$Uptake\ (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \qquad (1)$$

Pervaporation measurements

The pervaporation is a technique of continuous non-chromatographic separation, integrating the processes of evaporation and gas diffusion in a single step. It is a process used for separating mixtures by selective permeation through membranes, where a component of the liquid mixture preferably passes through a face of the membrane to the other, going to the gas phase[31]. Measures of SPEEK/TiO_2 membranes pervaporation were performed using 20 wt% ethanol solution in deionized water and pure deionized water. The apparatus was mounted in the lab, according to described previously[31,32], using three cells in series, hoses and stainless steel connections. The specific flux permeated in pervaporation measurements are typically obtained under steady state conditions using vacuum on the underside of the membrane and at constant composition and flow of the liquid at the top of the membrane. The permeated fraction is collected by traps frozen in liquid nitrogen. The result is the permeate flux in hybrid membranes.

X-ray diffraction studies (XRD)

XRD patterns of SPEEK/TiO_2 dry membrane samples were recorded in the 2θ range 2-80° at a scan rate of 5° min[-1] with Rigaku Miniflex II X-ray diffractometer, using Cu Kα (λ=1.5418 Å) radiation filtered through Ni.

Fourier transform infrared (FTIR) spectroscopy

The ATR-FTIR spectra were recorded in transmittance mode using a Perkin Elmer FTIR spectrometer model 1720X, in the range of wavenumbers 4000–400 cm^{-1}. All the spectra were measured at a resolution of 2 cm^{-1} and 20 scans.

Thermal gravimetric analyses

Thermal gravimetric studies (TG/DTG) were performed in a TA TGA Q500 from 25 to 800 °C at a heating rate of 10 °C/min and carried out under nitrogen flow 60 mL/min.

Proton conductivity measurements

The proton conductivity of SPEEK/TiO_2 hybrid membranes were evaluated by electrochemical impedance spectroscopy (EIS) (also known as AC impedance) based on through-plane method, where membrane is pressed between two stainless steel electrodes with the contact area of 0.1 cm². AC impedance spectra were recorded a frequency range of 1 MHz to 10 Hz with amplitude of 5 mV using an Autolab PGSTAT-30 potentiostat/galvanostat instrument. The resistance value associated to membrane conductivity was determined from the high frequency intercept of the impedance with the real axis (Z'). The proton conductivity (σ) was calculated from the impedance data according to Equation 2:

$$\sigma = \frac{L}{R\,S} \qquad (2)$$

where, σ is the proton conductivity (S.cm^{-1}), L is the membrane thickness (cm), R is the measured membrane resistivity (Ohm) and S is the cross-sectional membrane area perpendicular to current flow (cm²). All measurements were performed in ethanol solution 20 wt% in deionized water at different temperatures (30, 50, 80 °C).

Table 1. Ethanol and water uptake measurements at different temperatures.

Samples	Ethanol uptake[a] (%)			Water uptake[b] (%)		
	30 °C	50 °C	80 °C	30 °C	50 °C	80 °C
SPEEK 58 + 2% TiO₂	54.2	747.9	c	17.6	14.7	811.7
SPEEK 58 + 4% TiO₂	17.5	292.5	1185	12.7	6.4	653.2
SPEEK 58 + 6% TiO₂	10.2	159.2	1073	4.2	4.1	702.1
SPEEK 58 + 8% TiO₂	21.6	72.9	413.5	13.3	13.2	377.7
SPEEK 58 + 10% TiO₂	10.2	25.6	376.9	2.6	5.1	223.1
SPEEK 58 + 12% TiO₂	0	17.2	245.7	8.8	11.7	55.8

(a) Ethanol solution 20 wt% in deionized water, (b) deionized water and (c) sample dissolved.

Table 2. Specific permeated flux[a] of SPEEK membranes in ethanol[b] at 30 °C.

Samples	Specific permeated flux $(Kgm^{-1}h^{-1})$
SPEEK 58	8.8×10^{-3}
SPEEK 58 + 2% TiO₂	2.5×10^{-3}
SPEEK 58 + 4% TiO₂	1.2×10^{-4}
SPEEK 58 + 6% TiO₂	1.3×10^{-4}
SPEEK 58 + 8% TiO₂	1.1×10^{-4}
SPEEK 58 + 10% TiO₂	4.5×10^{-5}
SPEEK 58 + 12% TiO₂	4.1×10^{-5}
Nafion® 117	$\times 10^{-4}$

(a) The permeated flux unit is $(kgm^{-2}h^{-1})$. The specific permeated flux takes into account the thickness of the sample. Therefore, its units $(kgm^{-1}h^{-1})$. (b) Ethanol solution 20 wt% in deionized water.

Results and Discussions

Sulfonation is known to enhance hydrophilicity by introducing the SO_3H groups. The presence of sulfonic groups in aromatic PEEK polymers in 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[24].

The uptake measurements were performed separately in deionized water and ethanol solution 20 wt% and showed the structural behavior of hybrid polymeric material under fully hydration conditions. It is important to know the state of water (free water, freezable bound water and non-freezable bound water) in the membrane because the proton conductivity strongly depends on the water content[6]. The results presented in Table 1 clearly show the influence of the TiO_2 content in SPEEK matrix, where the uptake decreases with increasing of TiO_2 content.

This behavior can be explained by the possible appearance of a three dimensional network promoted by cross-links between the titanium oxide and SPEEK polymer matrix. These results are important because they provide an idea of dimensional stability of hybrid membranes under operation conditions and show trends in behavior as the barrier properties and permeability to ethanol. Thus the free volume of polymer material decreases, making the more tortuous path by ethanol due to inorganic phase presence and possible TiO_2 particles formation by sol-gel method. This trend can best be seen in pervaporation measurements.

Table 2 shows relationship between TiO_2 content and ethanol permeability. As on ethanol uptake, specific permeated flux of ethanol solution 20 wt% at 30 °C decreased with increasing of TiO_2 content, following the trends observed in uptake measurements. This behavior suggests the improvement in barrier properties probably due to cross-linking of the hybrid membranes and possible titanium oxide particles growing.

For comparison, specific permeate flux of ethanol in Nafion® 117 was measured under similar experimental conditions and the results showed a value ten times greater than SPEEK 58 + 10% and 12% TiO_2 sample, for example. These results are consistent with Kalappa and Lee[20], showing that the hybrid membranes of SPEEK/TiO_2 have a special feature of permeability to alcohols, not only due to the polymer, but also from the possible cross-linking action and TiO_2 particles presence (physical barrier), as previously suggested by the results of ethanol uptake.

X-ray diffraction patterns of SPEEK 58, as well as composite membranes, are given in Figure 1. PEEK is a semicrystalline polymer, showing sharp crystalline peaks, corresponding to (110), (111), (200) and (211) planes, in the 2θ range of 20-30°[33,34]. Sulfonation strongly decreases crystallinity and highly sulfonated SPEEK is reported to be totally amorphous[35,36]. However, the XRD pattern of SPEEK used in the present study indicates the presence of a crystalline peak, probably that due to the (110) plane, which is overlaid on a broad amorphous halo. The introduction of SO_3H groups into the PEEK alters the chain conformation and packing, and thus causes loss of crystallinity.

Since crystallinity of SPEEK is initially reduced in the composite membranes due to TiO_2 incorporation and a broad halo shifts to small angle, it can be safely stated that crystallinity of the composite membranes is more or less comparable with that of pure SPEEK 58.

IR spectra of SPEEK 58, as well as hybrid composite membranes are shown in Figure 2. The broad-band in SPEEK 58 samples appearing at 3449 cm⁻¹ was assigned to O–H vibration from sulfonic acid groups interacting with molecular water. The aromatic C–C band at 1491 cm⁻¹ for PEEK is normally observed to split due to substitution upon sulfonation. An absorption band at 1080 cm⁻¹ in SPEEK 58 was assigned to sulfur–oxygen symmetric vibration O=S=O. The absorptions at 1219, 1076, and 1020 cm⁻¹ were assigned to the sulfonic acid group in SPEEK 58[37]. The absorption at 709 cm⁻¹ was attributed to S–O stretch vibration. It is important to note
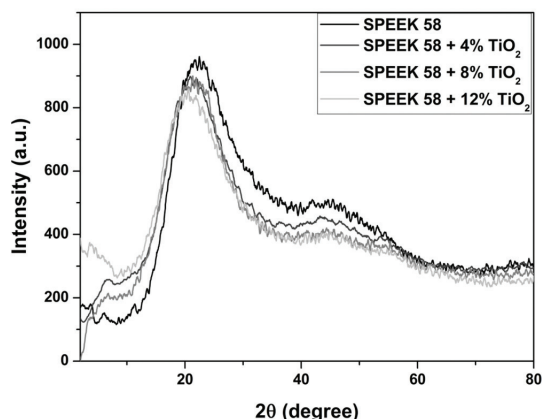
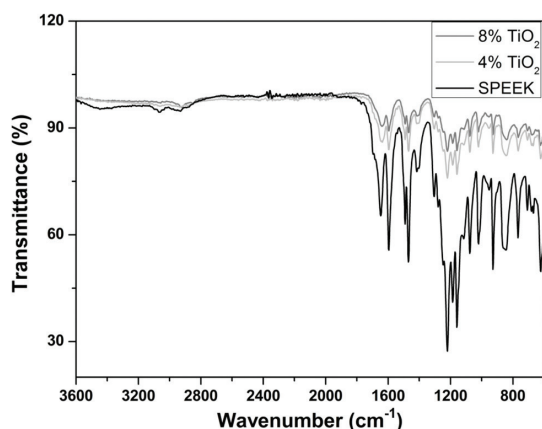**Figure 1.** XRD pattern of composite membrane samples.

Figure 2. FTIR spectra of hybrid composite membranes.

Figure 3. TGA curves of organic-inorganic composite membranes.

Table 3. Main degradation temperatures of SPEEK/TiO$_2$ membrane samples.

Sample	Temperature degradation (°C)	
	SO$_3$H	backbone chain
SPEEK 58	**300**	**537**
SPEEK 58 + 2%	**313**	**524**
SPEEK 58 + 4%	**350**	**515**
SPEEK 58 + 6%	**349**	**516**
SPEEK 58 + 8%	**348**	**507**

that the broad-band of O–H vibration was less intense, probably due to TiO$_2$ incorporation. Furthermore, all main absorption band intensities in SPEEK/TiO$_2$ membranes decreased in relation to SPEEK 58. This trend suggests that TiO$_2$ incorporation possibly occurs by interactions between TiO$_2$ and sulfonic groups. That would explain the observed behavior by uptake and pervaporation measures.

Thermo gravimetric analysis was performed for all hybrid composite membranes. In comparison with pure PEEK, which exhibits a single step thermal degradation, SPEEK 58 has two distinct steps Figure 3[38]. For all samples the first weight loss, up to 200 °C, can be due to the evaporation of residual solvents, mainly NMP, solvent in which the reactions were performed.

The second thermal degradation temperature of SPEEK normally decreased and the signal broadened with degree of sulfonation. The second main weight loss step is attributed to the decomposition of the SO$_3$H groups in the range of 300-350 °C. The last weight loss step in all samples is due to the pyrolysis of the polymer backbone chain in the range of 500-540 °C (Table 3).

The increase of second degradation temperature of SPEEK/TiO$_2$ membranes probably indicates that occurs a thermal property improvement in fact, mainly due to interaction between sulfonic groups of SPEEK 58 and
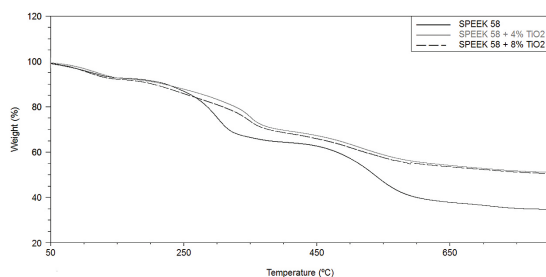
polar groups of titanium oxide that change the sample microstructure. This behavior corroborates with the FTIR results and the hypothesis previously discussed. The chelation reaction with acac may in fact lead to a less branched inorganic polymer. A lower degree of branching of the polymeric chain would result in an increased concentration of hydroxyl moieties that, in turn, leads to an increased density of electrostatic interactions and hence to an improved stability[19].

The proton conductivity of polyelectrolytes is strongly dependent on the hydration level of membranes[39], thus the determination of the electrochemical behavior of new materials at different water content is basic and primordial at first. In this context we measured the membrane proton conductivities at different temperatures and with different TiO$_2$ contents, which resulting in different values of water uptake. Proton conductivity data for different hybrid membranes are presented in Table 4.

Generally, two principle mechanisms of proton conductivity, Vehicle mechanism and Grotthuss mechanism (hopping) describe proton diffusion through the membrane. It is possible that the bound water participates by the Grotthuss mechanism, and the free water takes part mostly by vehicle mechanism[39-41]. It shows that the enhanced proton conductivity is attributed to the retention of water. In this case, the addition of TiO$_2$ provides more protons to the hybrid material. The results showed that proton conductivity of SPEEK/TiO$_2$ membranes increased with increasing of TiO$_2$ content. It is a clear indication that TiO$_2$ content is responsible for the proton-conducting behavior of SPEEK/TiO$_2$ system. Titanium oxide and SO$_3$H acid groups might be suitable for migration via the strong acid sites mainly on the internal surface, and the hybrid membrane can have lower resistivity in SPEEK58 + 8% TiO$_2$ samples (Figure 4). According to Kreuer[42] SO$_3$H acts as the Brønsted acid by water of hydration, that is, in general, weakly bound structure, resulting in high conductivity.

Table 4. Proton conductivities of SPEEK/TiO$_2$ membranes.

Sample	Proton conductivity (mS.cm^{-1})		
	30 °C	50 °C	80 °C
SPEEK 58	36	dissolved	dissolved
SPEEK 58 + 4%	N.R	25	114
SPEEK 58 + 8%	N.R	25	172
SPEEK 58 + 12%	N.R	14	59

N.R - not realized.
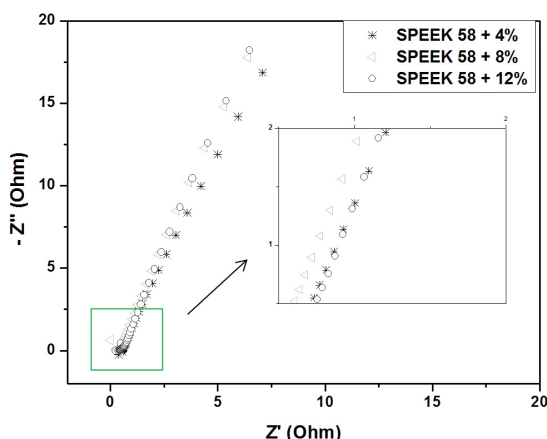
Figure 4. Complex impedance spectra (Nyquist plot) of membranes in ethanol solution 20 wt% at 80 °C.

Consequently, the conductivity of SO$_3$H is closely related to the number of water molecules coordinated to the SO$_3$H/TiO$_2$ complex.

However, water state studies (by DSC, for example) are needed to elucidate the mechanism of proton conduction of these systems due to the difficulty on quantification of each state of water. In some cases, bound water can be classified into freezing bound water and non-freezing bound water, which is due to a weak or a strong interaction, respectively, between the water molecules and the polymeric matrix with polar and ionic groups. On the other hand, we noted that the proton conductivity decreases with TiO$_2$ content above 8 wt%. This behavior is justified as the TiO$_2$ acts as cross-linking agent. As previously described in the uptake and pervaporation measurements, a possible increase in crosslink density improves the barrier properties, directly influencing the decrease in proton conductivity.

Conclusions

A series of hybrid membranes have been prepared by incorporation of titanium oxide into poly(ether ether ketone) polymer matrix by sol-gel *in situ* method. The PEEK sulfonation was confirmed by ATR-FTIR spectra. The presence of titanium oxide was observed by thermo-gravimetric analysis. The swelling behavior of hybrid membranes was significantly reduced with increasing TiO$_2$ content. The proton conductivity of SPEEK/TiO$_2$ hybrid membranes was in the order of 10^{-3} S cm^{-1} and increased with TiO$_2$ content, except for the membranes showed low absorption in ethanol. The best conductivity (172 x 10^{-3} S cm^{-1}) at 80 °C in ethanol was obtained for

membranes containing 8 wt% of TiO$_2$ by electrochemical impedance spectroscopy. The specific permeate flux of the hybrid membranes on pervaporation process was about one order of magnitude lower than that obtained in Nafion® 117 membrane. The ethanol permeability decreased with increasing content of titanium oxide, being lower than those in Nafion® 117 at all temperatures. Similar trends in ethanol uptake, ethanol permeability and the increase of second degradation temperature of SPEEK/TiO$_2$ membranes suggest the existence of intermolecular hydrogen bonding interaction between SO$_3$H side chain of SPEEK and TiO$_2$. These specific interactions are considered to be responsible for continuous drop in water and ethanol uptake with titanium oxide and ethanol permeability near and beyond the critical content level. The advantage of SPEEK/TiO$_2$ hybrid membrane in terms of low ethanol permeability is particularly attractive for direct ethanol fuel cells applications.

Acknowledgments

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