

COMPOSITE MEMBRANES BASED ON SPEEK FOR PROTON EXCHANGE MEMBRANE FUEL CELLS

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Introduction

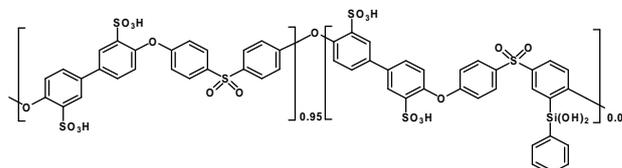
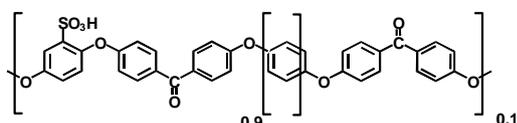
The development of new proton conducting materials is a key issue for the exploitation of the full potential of Polymer Electrolyte Membrane Fuel Cells (PEMFCs) as energy conversion devices. To successfully perform, the electrolytes must meet several requirements: high proton conductivity even at low values of relative humidity, reduced methanol crossover, high hydrolytic stability, high oxidative resistance, good mechanical properties at temperatures higher than 100 °C and, possibly, low cost.

In our laboratories, attention has been focused on possible modifications that can be introduced in sulfonated arylene main chain polymers, in particular polyether etherketone (PEEK) and polyphenylsulfone (PPSU). Both polymers show rather large conductivity when sulfonated, but their mechanical, solubility and morphological properties progressively deteriorate with the degree of sulfonation (DS), because acid groups directly linked to the aromatic hydrophobic backbones cannot assemble in phase separated domains.

The introduction of an inorganic dopant into the ionic conductor may stabilize the polymeric phase, overcome the temperature barrier limit and reduce fuel crossover [6]. The main objective in the development of these composite hybrid membranes is to improve the mechanical strength of the material without sacrificing important polymer properties necessary to operate in FCs.

We present here two approaches for development of composite materials: i) *in situ* formation or dispersion of inorganic components, such as nanometric TiO₂, in SPEEK matrix and ii) dispersion of a second hybrid phase, sulfonated and silylated PPSU, in SPEEK matrix. The expected improvements will be checked in the two cases.

The representation of SPEEK and SiS-PPSU is as follows:



Experimental

Synthesis of sulfonated PEEK

Sulfonated PEEK was prepared by reaction of PEEK (Victrex 450P, MW = 38300) with concentrated sulfuric acid at 50°C for different times to obtain different degrees of sulfonation (DS). The degree of sulfonation was evaluated both by ¹H NMR [1] and by titration.

Synthesis of Silylated PPSU (SiPPSU)

SiPPSU can be obtained by metalation reaction of PPSU with butyl-lithium (BuLi), followed by electrophilic substitution by phenyl-trichlorosilane (PhSiCl₃). The characterization of SiPPSU was already reported. [8]

The synthesis of SiS-PPSU was made in two steps: i) metallation reaction with butyl-lithium followed by electrophilic substitution with phenyl-trichlorosilane, ii) hydrolysis and reaction with concentrated sulfuric acid, giving a very high DS = 2, determined by elemental analysis [8].

Membrane casting

The procedure for membrane preparation was solution casting using dimethylsulfoxide (DMSO). In a typical experiment, around 250 mg sample were prepared by dissolving 93w% SPEEK with DS = 0.75 or 0.9 in 30 mL of solvent and 7w% SiPPSU was added and sonicated for 48 hours. The suspension was cast onto a Petri dish and heated to dryness. The resulting membranes were treated under dynamic vacuum 24 h at 80°C for solvent removal. Subsequent thermal treatments of membranes were performed at 140°C for 64 h.

Composite membrane via *in situ* procedure

A sol prepared adding Ti(OBu)₄ was added to a solution of SPEEK in DMAc. The solution was then cast onto a Teflon plate and heated to dryness. The amount of Ti(OBu)₄ was calculated to produce samples containing 95:5 wt % SPEEK/TiO₂. The membranes were activated in 5 M H₂SO₄, rinsed with water and dried in vacuum at 100 °C for 10 h.

Results and Discussion

Thermal behavior

Figure 1 shows a typical TG curve of a blend SPEEK/TiO₂ membrane. The first mass loss below 150°C can be attributed to residual solvent removal. The second weight loss, between 250 and 300 °C, corresponds to the decomposition of sulfonic groups. Complete pyrolysis occurred above 400 °C. The thermal stability is fully compatible with intermediate temperature fuel cell operation.

Mechanical properties

Elastic modulus E , maximum strength σ and % elongation at rupture ε were determined by tensile stress-strain tests. Figure 2 shows typical stress-strain curves obtained for three different silylated and sulfonated membranes.

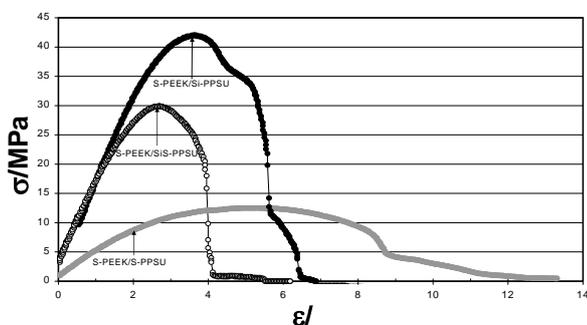


Figure 2. Stress-strain curves for composite polymer membranes.

The data show that whereas sulfonation of PPSU softens the polymer, silylation of PPSU enhances the membrane strength. The presence of the dispersed Si-PPSU second phase strongly enhances the membrane elastic modulus. The mechanical strength of polymer electrolyte membranes has been related to their water uptake and swelling.

Water sorption characteristics

The number of mol of water absorbed per mol of acid group (λ) increases almost linearly with time for pure SPEEK, leading to dissolution of the sample, while for composites λ reaches asymptotically a limit of ca. 9.

The water sorption isotherm is represented in Figure 3. A hysteresis between sorption and desorption branches can be observed, corresponding to water condensation into membrane pores. The water uptake coefficients at high RH are consistent with the value obtained after full immersion in water for S-PEEK/Si-PPSU.

Fig 2 shows an almost steady value

$\sigma_{\perp} \approx 0.08 \text{ S cm}^{-1}$ at increasing RH, whereas σ_{\parallel} is a monotonic increasing function of RH. This experimental evidence suggests that the water uptake occurs with a surface gradient concentration of water, whose depth profile is steadily decreasing from the surface to the bulk. It is known that the water uptake process is activated by the hydrophilic groups or the adsorbing surface of the oxide particles; however the presence of water creates elastic tensions within the membrane that cause progressive swelling and then limit the increasing of its bulk concentration. The Fig 2 indicates therefore that during the initial stages of water uptake, both surface and bulk concentrations increase in analogous way; yet, near to saturation concentration increases slower in the bulk than at the surface, due to the easier deformability of the membrane.

Proton conductivity

The conductivity of the polymeric electrolytes is strongly dependent on the level of hydration of the membranes. Thus, the determination of the electrochemical behavior at different water content is necessary for a first screening. To have information on the membrane dimensional stability we measured the normal, σ_{\perp} , and tangential, σ_{\parallel} , proton conductivities at different RH values at 100 °C. The former, measured with the electric field perpendicular to the surface, depends on the bulk properties of the membrane; the latter was determined by four-probe impedance measurements. The observed differences can be associated with membrane swelling phenomena, determined by the increasing of hydration [9].

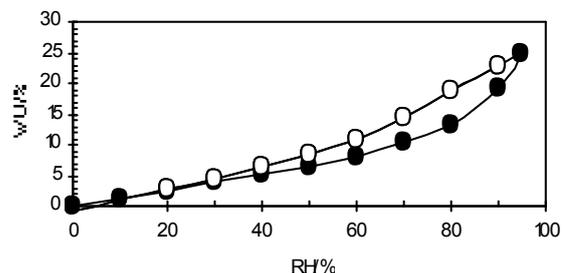


Figure 3. Water sorption/desorption isotherm at 25°C for S-PEEK/Si-PPSU composite polymer membranes. Sorption: ●, desorption: ○.

[1] S. M. J. Zaidi, S. D. Mikhailenko, G. P. Robertson, M. D. Guiver and S. Kaliaguine, *J. Membr. Sci.*, 173 (2000) 17.