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Mechanical properties and morphology of polystyrene-co-acrylic acid synthesized as membranes for fuel cells

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ABSTRACT

Two copolymers of poly(styrene-co-acrylic acid) (PS-AA) were synthesized in solution by radical polymerization and partially crosslinked by adding, either trimethylol propane trimethacrylate (TMPTMA) or divinylbenzene (DVB) to improve mechanical resistance. Copolymers were sulfonated with theoretical molar quantities of sulfuric acid ($H_2SO_4 = 170\%$) and two different amounts of silver sulfate ($Ag_2SO_4 = 0.11$ or 0.055%). Materials were dissolved in three different solvent compositions: copolymer + THF, copolymer + THF+55% DMSO and copolymer + THF+110% DMSO and used to prepare membranes prepared by casting. Membranes were characterized by Thermomechanical Analysis (TMA), Scanning Electron Microscopy (SEM), Ionic Exchange Capacity (IEC) and Water Uptake (WU) capacity. Addition of DMSO to THF during casting procedure has an important increment on IEC and WU results; however, mechanical resistance is considerably reduced. SEM images show almost no pores in the membranes casted from THF alone, while increasing the amount of DMSO enhances porosity. Such phenomenon is responsible for reduced mechanical property (brittleness), as seen by TMA.

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Introduction

The most common and widely used membrane for PEM fuel cells is the Dupont's product Nafion, and it is also well known that it lacks for mechanical stability at temperatures of 80–100 °C. Moreover, it not useful for direct methanol fuel cells due to its permeability. Such drawbacks have induced a great interest in discovering new polymeric ionic materials for the preparation of ion exchange membranes. Traditionally, a

membrane is evaluated according to their polyelectrolyte performance, characteristics as ion exchange conductivity (IEC), water uptake (WU or U) and proton conductivity. However, membranes must also possess mechanical stability to withstand the processes to which they are exposed; those include processing (extrusion, casting, etc.), incorporation of catalysts, compression during formation of the MEA, pressure during PEMFC closure to test performance, dimensional changes during hydration and dehydration of the membrane, and pressure generated by the fuel, either gaseous or liquid.

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The mechanical properties of polymeric membranes depend on its own chemical nature as well as by some external factors. A polymeric material tends to be brittle if has low molecular weight, a rigid chemical structure or no branching. Furthermore, an increase in the degree of sulfonation, needed to improve water uptake and conductivity, reduces mechanical performance on the other side. The latter also reduce the long-term stability of the membrane in the fuel cell [1]. Mechanical degradation in polymeric membranes occur in many forms, such as cracks, tears, punctures, or pinhole blisters; all of them reducing their service life. Hence, adequate care must be taken with membranes during assembly of MEA to prevent no uniform pressure and between bipolar plates during operation [2].

Mechanical properties of Nafion are influenced by hydration, although high conductivities require the presence of moisture. Nevertheless, when Nafion is soaked in water or any solvent, its Young's modulus decreases, since the solvent have a direct impact on the stress–strain relationship. The high solvent (water) content enhance swelling of the membrane, reduces the intermolecular forces and increase the degree of elongation; such conditions make the Nafion membrane more ductile and susceptible to permanent deformation, gradual weakening, and eventual failure in fuel cell when exposed to pressure gradients and pressure pulses [3,4].

It has been reported [5] proton conductivity and methanol permeability ($T = 20\text{--}60\text{ }^{\circ}\text{C}$) for membranes cast from Sulfonated Poly(styrene) (SPS); the results showed that both properties depend on sulfonation degree. The sulfonated membrane (sulfonic acid groups content of about 15% mol) exhibited conductivity equal to that of Nafion. However the mechanical properties were not evaluated. Our research group has been working on sulfonated cheap hydrocarbon copolymers, based on styrene and acrylic acid, as PEM membranes for low temperature applications. Such copolymers are intrinsically rigid and brittle structures, which mechanically improve after partial crosslinking with byfunctional (divinylbenzene-DVB) or a tryfunctional (trimethylolpropane trimetacrylate-TMPTMA) agent [6,7], including their degradation reactions evaluated during sulfonation procedure [8]. Considering all the above aspects, it is of high importance the evaluation of mechanical properties for new synthesized materials, alternative to Nafion, pretending to be employed as ion exchange membranes.

Experimental

Materials

Styrene monomer (St, 99%, Aldrich) was purified with NaOH, dried with CaCl_2 and distilled at reduced pressure. Acrylic acid monomer (AA, 99%, Aldrich) was added with phenothiazine and distilled at reduced pressure. Benzoyl peroxide (BPO, Aldrich). Nafion 117 membrane (Aldrich), Sulfuric acid 98% (J.T.Baker), Hydrochloric acid 36.5–38% (Sigma Aldrich), Nitric acid 70% (CTR Scientific), Silver Nitrate $\geq 99.0\%$ (CTR Scientific), Sodium chloride (J.T. Baker), Sodium hydroxide (Aldrich), inhibitor free Tetrahydrofuran $\geq 99.9\%$ (THF, Aldrich), Dimethylsulfoxide $\geq 99.5\%$ (DMSO, Sigma Aldrich) and anhydrous

dichloromethane $\geq 99.8\%$ (Aldrich). Trimethylol propane trimethacrylate (TMPTMA, Aldrich) and Divinyl benzene (DVB, Aldrich) as crosslinking agents.

Methods

Polymerization procedure

Two different copolymers of poly(styrene-co-acrylic acid) (PS-AA) were previously synthesized with 94% mol of St and 6% mol of AA. The reactions were carried out by conventional solution free radical polymerization, using diethylbenzene as solvent. Benzoyl peroxide was used as radical initiator at 0.045% mol, and partially crosslinked (crosslinking agent at 0.25% mol) with divinylbenzene (DVB) or trimethylol propane trimethacrylate (TMPTMA) to improve the mechanical resistance. The initiator and crosslinking agent concentrations used were selected from previous experiments made in our research group. The random PS-PAA copolymer D (crosslinked with DVB) exhibits a $M_n = 68,012$, $M_w = 259,095$, and the random PS-PAA copolymer T (crosslinked with TMPTMA) presents a $M_n = 54,068$, $M_w = 302,607$. The polymerization procedure was described and reported previously [8].

Sulfonation procedure

D and T copolymers were sulfonated with a theoretical molar quantity of sulfuric acid ($\text{H}_2\text{SO}_4 = 170\%$ mol) employing silver sulfate as catalyst ($\text{Ag}_2\text{SO}_4 = 0.11$ or 0.055% mol). Each copolymer was dissolved in dichloromethane by means of stirring at 200 rpm and $40\text{ }^{\circ}\text{C}$ during 40 min under nitrogen atmosphere. The theoretical amount of Ag_2SO_4 was dissolved in the H_2SO_4 and subsequently added to the dissolved copolymer, the sulfonation reaction was left to proceed during 2 or 4 h (for T and D copolymer, respectively). The reaction was ended removing the solvent and adding cold distilled water. The sulfonated copolymer was washed with more distilled water until reaching $\text{pH} \approx 7$. Finally, the polymer was dried at room temperature with an airstream during 48 h.

Casting procedures

Three membranes were prepared by casting from each copolymer, employing a specific solvent or mixture of solvents. The ratio copolymer mass/solvent volume/area membrane employed was $0.4\text{ g}/2\text{ mL}/16\text{ cm}^2$. The composition for the first casting was: sulfonated copolymer + THF; the second was sulfonated copolymer + THF + DMSO (55 % wt.) and the third was sulfonated copolymer + THF + DMSO (110 %wt). Evaporation of the solvent proceeded gradually at room temperature during 7 days, keeping the molds partially covered to allow solvent vapor to escape. Membranes thickness ranged from 0.18 to 0.22 mm, quite similar to Nafion's membrane (0.18 mm).

Membrane activation

Membranes were activated before further characterization. The membranes were unmolded and immersed in distilled water by two days, changing the water every 4 h to eliminate the DMSO. Subsequently, the membrane was immersed in HNO_3 0.5 M during 24 h, then immersed 1 h in H_2O_2 (5% vol) at $80\text{ }^{\circ}\text{C}$, 1 h in H_2SO_4 0.5 M at $80\text{ }^{\circ}\text{C}$ and finally 1 h in distilled water at $80\text{ }^{\circ}\text{C}$.

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