

Hybrid ion-exchange membranes for fuel cells and separation processes

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Abstract

This work reports the preparation and characterization of hybrid membranes cast from dispersions of inorganic fillers in sulfonated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene solutions. Silica gel, SBA-15 and sepiolite, all of them functionalized with phenylsulfonic acid groups, were used as fillers. For comparative purposes, the performance of composite membranes cast from dispersions of functionalized inorganic fillers in Nafion[®] solutions was investigated. Inspection of the texture of the membranes by using SEM techniques shows that the fillers are better dispersed in sulfonated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene than in Nafion[®]. The value of the water uptake for the membranes prepared from the former polyelectrolyte is in most cases at least three times that measured for hybrid Nafion[®] membranes. The conductivity of the membranes was measured at 80 °C by impedance spectroscopy obtaining values of 3.44, 6.90 and 3.54 S m⁻¹ for the hybrid membranes based on the triblock copolymer containing functionalized silica gel, SBA-15 and sepiolite fillers, respectively. These results compare very favourably with those obtained at 80 °C for Nafion[®] hybrid membranes containing silica gel, SBA-15 and sepiolite, all of them functionalized with phenylsulfonic acid groups, whose conductivities are, 2.84, 6.75 and 3.31 S m⁻¹, respectively. Resistance measurements carried out under controlled humidity conditions show that the conductivity of sulfonated triblock copolymer membranes containing functionalized SBA-15 filler undergoes a rather sharp increase when they are conditioned under an atmosphere of 75%, or larger, relative humidity.
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1. Introduction

The characterization of proton transport in ion-exchange membranes using impedance spectroscopy is a flourishing field of research which complements other well-documented studies reported in the literature related to concentration potentials, determination of counterion and coion transport numbers, diffusion coefficients, electro-osmotic permeability, etc. [1]. A better understanding of the relationship between structure and both conductivity and permselectivity is paramount to optimize the application of ion-exchange membranes as electrolytes for both low temperature fuel cells and ionic separation processes.

The relatively low protonic conductivity under low humidity conditions and the relatively high permeability to methanol are the main drawbacks that commercial cation exchange mem-

branes present in their use as polyelectrolytes in fuel cells technology. Moreover, good performance fuel cells require that membranes combine good mechanical properties and thermal stability, at moderately high temperatures. However, even high thermal stability ion-exchange membranes may undergo oxidative processes that preclude their use in the unfriendly working conditions of fuel cells. Several strategies, mainly focused in reducing the methanol uptake while preserving the water content and the high proton conductivity at working temperatures of about 150 °C, were used in the development of organic polyelectrolytes in recent years [2–5]. The strategies involve reinforcement of commercial ion-exchange membranes, such as Nafion[®], and synthesis of new membranes. The incorporation of suitable inorganic fillers into commercial cation exchange membranes seems to be a promising way of obtaining solid electrolytes for medium temperature fuel cells [2–4,6–9]. Fillers, such as silica, heteropolyacids, laminar metallic phosphates particularly layered zirconium phosphates [10–12] and phosphonates (phosphates functionalized by acid organic substituent [13]) improve the high temperature conductivity of Nafion[®] membranes.

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Aside high permeability to methanol, high cost is one of the major disadvantages of membranes based on perfluorocarbon ionomers. Hence, efforts are being made to develop cation-exchange membranes based on cheap materials. Block copolymers made up of hard and soft components are obvious candidates [14–19]. In this context, the preparation of cation-exchange membranes from poly(styrene-block-ethylene-co-propylene) [20] and hydrogenated poly(butadiene–styrene) copolymers [21,22] has been reported. Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (PSEBS) is a triblock copolymer made up of a thermoplastic phase (polystyrene) dispersed in an elastomeric matrix (polyethylene/butylene). Polyelectrolytes can be obtained by direct and selective sulfonation of the phenyl groups of the polystyrene component of the copolymer [23,24]. Recently Sangeetha [25] reported a thorough study on the conductivity and thermal properties of sulfonated PSEBS (SPSEBS) showing that fully hydrated membranes exhibit an excellent conductivity, of the order of 10 S m^{-1} . Moreover the thermal stability of SPSEBS membranes seems to improve by impregnating them with tetraethyl orthosilicate [26].

Pursuing in this line of research, this work reports the preparation of inorganic–organic hybrid membranes by incorporating inorganic materials containing phenylsulfonic acid groups into SPSEBS membranes. Attention is paid to the study of the effect of the fillers on the conductivity and mechanical and thermal stability of the membranes. For comparative purposes, the performance of Nafion[®]/fillers composite membranes is also investigated.

In this study, the membranes were characterized by measuring water uptake, ion-exchange capacity and conductivity. The homogeneity of the dispersion of the fillers in the membranes was analysed by SEM techniques, and the dynamic mechanical behaviour of the composites was studied at several frequencies in a wide temperature window. Comparison of the conductivities of the SPSEBS membranes with those of Nafion[®] leads to conclude that the former membranes exhibit interesting transport properties as solid electrolytes for fuel cells, as well as for separation processes based on membranes technology.

2. Experimental

2.1. Materials

Tetraethoxy silane (TEOS) (ABCR), phenyl-tri-ethoxy-silane (ABCR), triblock copolymer Pluronic 123 (Aldrich), silica gel 0.04–0.063 mm size (Merck), sepiolite Pansil-2 (Tolsa), toluene (Merck), hydrochloric acid (Merck), isopropanol (Scharlau), fuming sulfuric acid 65% SO_3 (Merck) were used as received.

Calprene H6120, a linear triblock copolymer of polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (styrene 32%), was a gift from RepsolYPF (Spain). A 5% solution of Nafion 117 in low molecular weight alcohol was supplied by Fluka.

2.2. Functionalization of inorganic materials

Phenyl residues were anchored to inorganic fillers by reaction of their hydroxyl groups with phenyl-tri-ethoxy-silane. In the case of silica gel, 5 g of this product were dispersed in 150 ml of toluene. Then 2.4 g of phenyl-tri-ethoxy-silane (2 mmol g^{-1} silica) and 250 μl of distilled water were added to the dispersion, and the mixture was stirred at 100°C , under reflux, for 24 h. The solid was filtered and successively washed with petroleum ether and ethylic ether, and finally dried in vacuum.

Anchorage of phenyl groups to SBA-15 was carried out by dissolving 4 g of Pluronic123 surfactant in 160 ml of an aqueous solution of hydrochloric acid (pH 1.5). Then the solution was added dropwise to a mixture of 8.41 g of TEOS and 1.06 g of phenyl-tri-ethoxy-silane, under vigorous stirring, until a transparent solution appeared. The solution obtained was transferred to a Teflon bottle, and 76 mg of NaF and 1 ml of distilled water were added to the solution, at 70°C , under stirring. The polycondensation reaction started immediately, and it was allowed to proceed for 2 days, under heating and stirring. The solid obtained was filtered and washed. The template was removed by Soxhlet extraction with ethanol during 24 h [27].

The first step of the functionalization of sepiolite was carried out by successively adding 2.5 mmol of phenyl-tri-ethoxy-silane and 1 g of sepiolite to 10 ml of a solution (1:1, v/v) of HCl in isopropanol, under stirring. After 15 h of reaction at 65°C , the solid was filtered and washed with methanol, methanol/water, distilled water, and dried at 90°C [28].

The phenyl groups of the moieties anchored to the fillers were finally sulfonated with fuming sulfuric acid as illustrated in the reaction scheme shown in Fig. 1.

2.3. Sulfonation of PSEBS

PSEBS was sulfonated with acetyl sulfate prepared *in situ* by reaction of acetic anhydride with sulfuric acid in dichloroethane (DCE), at 0°C [29]. Acetyl sulfate was added dropwise to a 10% solution of the polymer in DCE, under nitrogen and vigorous stirring, keeping the temperature of the reaction at 80°C . The sulfonation reaction was stopped after 4 h by adding isopropanol to the reaction medium. The polyelectrolyte obtained (SPSEBS) was recovered by steam stripping using boiling water for the evaporation of DCE. Then the polyelectrolyte was filtered, washed with distilled water and dried in vacuum, at room

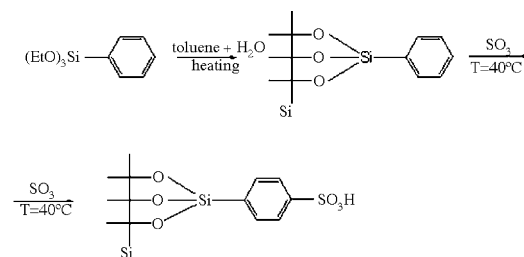


Fig. 1. Scheme showing the reaction of the $-\text{OH}$ groups of both silica gel and SBA-15 with phenyl-triethyl-siloxane and further sulfonation of the phenyl groups.

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