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# NMR investigation on nanocomposite membranes based on organosilica layered materials bearing different functional groups for PEMFCs

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## ABSTRACT

2D-layered materials are emerging as promising fillers for the preparation of high-performance composite membranes for PEMFCs systems combining excellent hydrophilic properties and thermal stability at high temperatures. Here we report the fabrication of a class of organosilica layered materials, bearing two different functional groups ( $\text{SO}_3^-$  and  $\text{PO}_3^-$ ), by a simple, one-pot thermal treatment. These materials were incorporated into the Nafion matrix for the preparation of hybrid electrolytes showing remarkable transport properties, especially at harsh conditions. Powder XRD and FT-IR reveal the complete exfoliation of filler's layers into Nafion matrix. Water dynamics investigation, carried out via NMR spectroscopy (diffusivity and relaxation times), demonstrates that the hydrophilic nature of synthesized filler leads to improved transport properties and water retention capacity of the composite electrolyte, particularly at high temperatures. Both Nafion composites exhibit considerable water diffusivity after several hours at 130 °C in “dehydrated” condition. The enhanced performances of the nanocomposite membranes are further confirmed by EIS investigation. The composite membrane containing 3% of sulfonated filler at RH 30% and 120 °C exhibits a proton conductivity value four times higher than the pristine polymer membrane. Finally, TGA and DMA analysis unveiled that the dispersion of silica layers into the polymer matrix produce a remarkable improvement in the thermal resistance of the electrolyte. The synergy between improved proton transport properties under dehydrated conditions and enhanced thermal resistance proposes these composite membranes as potential effective electrolytes able to extend the operating temperature of PEMFCs systems.

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## Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have attracted great technological interest as power sources for portable and vehicular applications [1,2]. As polymer membrane

electrolyte is one of the key components of these fuel cell systems, the Nafion membrane remains until nowadays the most widely used and studied electrolyte in literature [3]. Nafion matrix consists of the so called “Teflon-type” backbone [3,4] which contains perfluorovinyl ether side-chains with superhydrophilic terminal groups ( $-\text{SO}_3\text{H}$ , sulfonic acid) providing

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very attractive features such as high ionic conductivity (especially at low temperatures and fully hydrate state), excellent chemical, thermal and mechanical stability ideal for fuel cell applications [1,2,5]. Along these lines, considerable attention has been devoted to increasing the operation temperature so as to gain improved overall electrochemical reactions, carbon monoxide tolerance, and better water management [6,7]. The best way to achieve this is to develop electrolytes working above 100 °C via the introduction of hydrophilic fillers in the conventional membranes [8,9]. The presence of hydrophilic inorganic nanoparticles such as silica, titania, zirconia, clays, graphite oxide and heteropolyacids offer enhanced ionic conductivity but also improved thermo-mechanical properties to enrich the overall efficiency of PEMFCs [10–15].

Several groups have devoted significant efforts to the growth of hydrophilic groups such as  $-\text{PO}_3\text{H}$ ,  $-\text{SO}_3\text{H}$ ,  $-\text{COOH}$ ,  $-\text{OH}$  on inorganic nanoparticles' surfaces [16–18]. To that end, intensive functionalization steps have been involved in the synthetic process to increase the concentration of acidic (hydrophilic) functional groups and further enhancing the water retention and subsequently the proton conductivity of the resulting materials [19–21]. In the case of layered materials, this can be implemented by intercalation chemistry which involves the insertion of appropriate and robust organic species between the layers. So far, various layered nanostructures (such as graphene oxide [20], aluminosilicate layers [14], layered double hydroxides [22]) carrying various hydrophilic functional groups have already tested as nanofillers for the creation of innovative Nafion nanocomposites endowing enhanced proton conductivity, and excellent water retention capability.

Herein, we report a low cost and facile synthesis of a new class of silica layered materials decorated with the maximum possible loading of functional groups (sulfonate and phosphonate groups) in the solid state without any need of extra surface functionalization. These materials are finely dispersed in Nafion polymer matrix so as to create efficient nanocomposite membranes. Both materials found to enhance the proton conductivity and proton diffusivity especially in harsh conditions, while the silica substrate improves the thermal and mechanical properties of the final composite membrane. The hybrid membranes were structurally characterized by a combination of techniques (Powder X-ray Diffraction, IR spectroscopy, Thermogravimetric Analysis) while the mechanical properties of the polymeric membranes were tested by dynamic mechanical analysis in a wide temperature range. The proton conductivity properties of the membranes were evaluated at various relative humidities and different temperatures. Finally, the proton transport mechanism, one of the key aspects of the evaluation of these materials, was studied by Pulse-Field-Gradient NMR (PFG-NMR) technique to obtain a direct measurement of self-diffusion coefficients of water confined in the hydrophilic regions of the nanocomposites.

## Material and methods

### Synthesis of layered material

The synthetic procedure of Bourlinos et al. [23] was followed for the synthesis of phosphonated silica layered materials

(denoted as PSLM) and moving one step forward we synthesized for the first time sulfonated silica layered structures (SSLM). In brief, 3 g aqueous solution of appropriate silica precursor 3-(trihydroxysilyl)propyl methyl phosphonate, monosodium salt  $[(\text{OH})_3\text{Si}(\text{CH}_2)_3\text{OP}(\text{O})(\text{CH}_3)\text{O}^- \text{Na}^+]$  (50% w/w, Gelest) and 3-(trihydroxysilyl)propyl-1-propane-sulfonic acid, (30–35% in water, Gelest) filler were placed in an oven (at 80 °C for 5 days for PSLM and at 45 °C for 1 day for SSLM) until a xerogel is obtained. Then, DI water was added to the xerogel, and a milky suspension was obtained. The fine white powder was collected after successive washings (centrifugation parameters, 9000 rpm for 5 min) with water (5 times) and acetone (2 times) and dried at ambient conditions.

### Preparation of composite membranes

The composite membranes were prepared from 10 wt% Nafion solution (in a mixture of lower aliphatic alcohols and water) according to the following process: 1.5 g of Nafion solution was heated at 60 °C to remove all solvents and dissolved in 10 mL of DMF until obtaining a clear solution. Different loadings (1 and 3 wt%) of the silica layered material in DMF suspension were added drop-wise to the solution of Nafion, and the mixture was stirred at 60 °C to ensure complete mixing. Finally, the solution was cast on a petri-dish and left at 100 °C overnight, in order to obtain a homogenous membrane with approximately 70  $\mu\text{m}$  thickness. All composite membranes produced by casting method. The final membranes subsequently treated by rinsing in: (i) boiling  $\text{HNO}_3$  solution (1 M) for 1 h to oxidize the organic impurities, (ii) boiling  $\text{H}_2\text{O}_2$  (3 vol %) for 1 h in order to remove all the organic impurities, (iii) three times in boiling deionized  $\text{H}_2\text{O}$  for 10 min, (iv) boiling  $\text{H}_2\text{SO}_4$  (0.5 M) for 1 h to remove any metallic impurities, (v) boiling deionized  $\text{H}_2\text{O}$  for 10 min twice to remove excess acid, and soaking in (vi) EDTA solution (0.001 M) for 1 day, (vii) 2 M HCl at 80 °C for 2 h followed by boiling in fresh distilled water to remove any residual acids, (viii) repeating again the treatment with EDTA and finally, (ix) rinsing in boiling deionized water three times to remove any residual EDTA [14,24]. The fully hydrated membranes were stored at room temperature. The synthesis of composite membranes is shown schematically in Fig. 1.

### Material characterization

XRD patterns of all samples were recorded on a Rigaku R-AXIS IV Imaging Plate Detector mounted on a Rigaku RU-H3R Rotating Copper Anode X-ray Generator ( $\lambda = 1.54 \text{ \AA}$ ). The patterns were recorded in the  $2\theta$  range from 2 to 60°.

Infrared spectra were measured using a Thermo Scientific Nicolet 6700 FTIR equipped with a  $\text{N}_2$  purging system and a  $\text{LN}_2$ -cooled wide range Mercuric Cadmium Telluride detector in the mid-infrared region of 4000–400  $\text{cm}^{-1}$ .

TGA measurements were performed on approximately 15 mg of each sample using SETARAM SETSYS Evolution 18 Analyser, in the range of 25–850 °C, at a heating rate 5 °C/min in an  $\text{Al}_2\text{O}_3$  crucible under air flow (16 mL/min).

In-plane conductivity of membranes was measured by an impedance AC four-electrode system, adopting a commercial cell (BT-112, Scribner Associates Inc) fitted between the anode

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