Synthesis and characterization of novel hybrid polysulfone/silica membranes doped with phosphomolybdic acid for fuel cell applications

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ABSTRACT

Novel proton conducting composite membranes based on sulfonated polysulfone (sPSU)/SiO$_2$ doped with phosphomolybdic acid (PMoA) were synthesized, and their proton conductivity in acid solutions was evaluated. The hybrid membranes were prepared by casting and the characterization by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) and X-ray diffraction (XRD) confirmed the presence of the inorganic charges into the polymer. Thermal properties and proton conductivity were also studied by means of thermogravimetric analysis (TGA) and electrochemical impedance spectroscopy (EIS), respectively. The incorporation of the inorganic particles modified the thermal and mechanical properties of the sPSU as well as its proton conductivity. Taking into account that a compromise between these properties is necessary, the hybrid membrane with 2%SiO$_2$ and 20%PMoA seems to be a promising candidate for its application in proton-exchange membrane in fuel cells (PEMFCs) operated at high temperatures.

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1. Introduction

Nowadays, clean energy technologies play an important role in overcoming fossil fuel exhaustion and global pollution. Among these technologies, fuel cells are electrochemical energy systems that convert energy from a chemical reaction into electrical energy without emitting pollutants. In particular, the polymer fuel cells based on proton-exchange membranes (PEMFCs) are of great importance in the automotive field because of its higher energy efficiency and no emission compared to the combustion engines [1]. Currently, the most commonly used polymer electrolyte in PEMFC is based on expensive perfluorinated membranes, such as Nafion®, which present high proton conductivity, good mechanical strength and excellent stability. However, these membranes show several drawbacks since to ensure good proton conduction they must be fully hydrated, limiting their working temperature range below 80 °C and 100% relative humidity [2,3]. Moreover, this type of membrane exhibits high methanol permeability and high

cost of production, which limits its further application and future commercialization.

These limitations have led to research and develop different polymers as promising alternatives to improve fuel cell performance of the current perfluorosulfonic membranes. One research line involves the sulfonation of aromatic polymers with non-perfluorinated backbone such as polyaryl ether ketone [4], polystyrene [5] as well as polybenzimidazoles [6]. Among these polyaromatic materials, polysulfone (PSU) is a commercially available polymer and well known for its excellent mechanical, thermal and chemical stability [7]. Hybrid organic–inorganic nanocomposites have gained considerable attention because present improved properties such as swelling capacity, water retention or operating temperature, while maintaining mechanical properties [8–10]. In this line, there are several studies that reflect the improvement of performance of several polymers due to the incorporation of inorganic particles such as SiO$_2$ [11], TiO$_2$ [12] or zeolites [13]. Also, another inorganic fillers such as heteropolyacids like phosphotungstic (PWA), phosphomolybdic (PMoA), silicotungstic (SiWA) and silicomolybdic (SiMoA) acids related to the well-known Keggin structure, have recently received most attention due to their good proton conductivities [14–17]. However, it is well known that heteropolyacids itself are water soluble and may be easily extracted during the operation of fuel cell, leading to the instability of the composite membranes. For this reason, the retention of heteropolyacid into polymer matrix

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appears as one of the most challenge in preparing heteropolyacid-containing membranes. For this purpose, inorganic particles have been incorporated together these materials to immobilize them inside a polymer matrix [18]. Thus, the incorporation of SiO_2 nanoparticles showed that it is effective to reduce PWA leaching in sulfonated polysulfone nanocomposites membranes [19]. The aim of this work was the evaluation of novel proton-conducting composite electrolyte based on hybrid polysulfone/SiO_2 membranes doped with PMoA as possible alternative for current used PEMFC. Furthermore, sPSU/SiO_2 membranes containing different amounts of SiO_2, were also prepared for comparation.

2. Experimental

2.1. Materials

The polymer used in the study was polysulfone Udel (PSU) with $Mn=22,000$. The solvents were trimethylsilyl chlorosulfonate (TMSCS, 99%), 1,2-dichloroethane (DCE) and N,N-dimethylaceta-mide (DMAc). For the preparation of composites two inorganic compounds were used, pyrogenic silica (fumed silica, 99.8%) with an average particle size of 11 nm and surface area of 255 ± 15 m^2/g, and commercial phosphomolybdic acid ($H_3PMo_{12}O_{40}.xH_2O$, PMoA). All of these reagents were purchased from Sigma-Aldrich. Sulfonated product purification was carried out by adding ethanol (Panreac).

2.2. Sulfonation of polysulfone

Firstly, the sulfonation process was carried out in anhydrous conditions following the method described by Chao et al. [20]. Thus, a solution of polysulfone in DCE was prepared and purged with nitrogen for one hour. Then, a solution containing the sulfonating agent (TMSCS) and DCE was slowly added drop by drop under magnetic stirring. The resulting mixture was additionally stirred for 24 h at room temperature. Once the sulfonation process was completed, the product obtained was poured into ethanol. Finally, the precipitated polymer was filtered and washed with distilled water up to neutral pH.

2.3. Composite membrane preparation

All membranes were prepared by casting procedure. A solution consisting of 5 wt% of sPSU in DMAc was stirred for 2 h at room temperature and subsequently was filtered. For the preparation of sPSU/SiO_2 membranes, different amounts of SiO_2 nanoparticles (0.5, 1, 2, 4 and 6 wt%) were added and the resulting mixture was stirred for 1 h at 60 °C. Afterward, the solutions were placed in an ultrasonic bath at 60 °C for 1 h and finally they were magnetically stirred for an additional 1 h at room temperature. Subsequently, the solutions were filtered, added to a Petri dish and heated in order to remove the solvent.

On the other hand, for some SiO_2 doped membranes (2 and 4 wt%), the effect of the addition of the heteropolyacid was studied. In this case, different amounts of PMoA (10 and 20 wt%) were dispersed with SiO_2 in water. The resulting suspension was dried at room temperature and the obtained solid was crushed using an agate-mortar with the aim to obtain a fine powder. After that, the preparation of sPSU/SiO_2/PMoA composite membranes was carried out by the same mixing and thermal procedure used in preparation of sPSU/SiO_2 membranes aforementioned. As result, thick membranes between 80 and 140 microns were obtained.

2.4. Methods

2.4.1. ^{1}H-NMR analysis

The sulfonation degree of sPSU was estimated by means of liquid ^{1}H-NMR [21]. The analysis was performed on a Bruker Avance DPX 300MHz spectrometer using dimethylsulfoxide (DMSO-d$_6$) as the solvent and tetramethylsilane (TMS) as internal reference.

2.4.2. SEM

The morphology of prepared membranes was analyzed with a Philips XL30 scanning electron microscope operating at 15 kV and equipped with a backscattered-electron detector (BSE) and an energy-dispersive analyzer (EDAX 4i). In order to examine the cross-sections, the membrane samples were fractured cryogenically by immersion into liquid nitrogen and then coated with gold.

2.4.3. Infrared spectroscopy

Infrared characterization was performed using a Perkin-Elmer Spectrum GX Instrument (resolution 4 cm^{-1}) in the range of 4000–400 cm^{-1}. The infrared spectra of SiO_2 and PMoA powder were recorded in KBr pellets and composites membranes slices of about 50 microns of thickness were used for the analysis.

2.4.4. X-ray diffraction

X-ray diffraction (XRD) patterns were recorded on a Philips X'Pert diffractometer equipped with a CuKα radiation source. This instrument has a ($\theta/2\theta$) Bragg–Brentano geometry and is equipped with a curved graphite monochromator. The 2θ range analyzed was 5–55° with a step scan of 0.02° and a counting time of 2.8 s per step. Finally, the experiments were carried out at an excitation voltage of 40 kV and a current of 40 mA.

2.4.5. PMoA extraction

To evaluate the ability of silica nanoparticles to reduce the leaching of heteropolyacid in water, we have estimated the extraction of PMoA by means of UV–vis spectroscopy. The study was carried out in a Jasco V-650 UV–vis spectrophotometer. The sPSU/SiO_2/PMoA composites membranes were immersed in deionized water at room temperature for 72 h. After that, the solvent with extracted PMoA was placed into a quartz cell and then measured at 253 nm, which correspond to the maximum absorption of the studied heteropolyacid. Thus, the PMoA extraction (%) was determined by using the following equation [19]:

$$PMoA_{extraction}(\%) = \frac{C \times V}{M_{PMoA}} \times 100 \qquad (1)$$

where C is the extracted PMoA concentration obtained from the concentration–absorption graph.

2.4.6. Water uptake

Given that the water content affects the proton conductivity and mechanical properties of the membranes, the water uptake percentage was determined. For this purpose, the membranes were dried in a vacuum oven at 60 °C for 24 h until constant weight. Each dried membrane was subsequently weighed (W_{dry}) and soaked in distilled water at room temperature for 72 h. After that, the membranes were taken out and immediately weighed (W_{wet}) after removing the surface water. Water uptake was calculated using the following equation:

$$W_{uptake}(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \qquad (2)$$

where W_{wet} and W_{dry} are the weights of the wet and dry membrane, respectively.