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Synthesis and characterization of composite membranes modified with Halloysite nanotubes and phosphotungstic acid for electrochemical hydrogen pumps

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ABSTRACT

One of the main problems in electrochemical hydrogen pumps is the transport of protons, water retention and hydrogen crossover through the membrane. Considering prospects for an electrochemical hydrogen compression system, in this work, membranes based on Sulfonated Poly (Ether-Ether Ketone) (SPEEK) were made and modified with Halloysite nanotubes (HNT) and Halloysite nanotubes impregnated with phosphotungstic acid (PWA/HNT30) 15. These modified membranes were physicochemically characterized by scanning electron microscopy (SEM), X-Ray diffraction (XRD), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). It was found that the nanotubes were successfully incorporated by impregnating the heteropolyacid on the nanotubes. In addition, the membranes were characterized by swelling (area and volume) and W_{Up}, obtaining a slight decrease in these values. In contrast, the proton conductivity was increased by 42% and 88% for the membranes impregnated with HNTs and (PWA/HNT30) 15, respectively. Finally, the membranes were evaluated in a hydrogen pumping system, and lower energy consumption at $j = 0.4\ A\ cm^{-2}$ has been obtained.

1. Introduction

The electrochemical hydrogen pump (EHP) offers an efficient solution for hydrogen storage for use in fuel cells or as gas natural reforming technology to obtain high purity hydrogen. An EHP system is based on the following mechanism: Molecular hydrogen (H_2) at low pressure is injected into the proton exchange membrane fuel cell (PEMFC) anode compartment. When the H_2 makes contact with the anode, the molecule is oxidized, producing protons and electrons. This is achieved by a catalyst, usually Pt. While electrons travel to the cathode through an external circuit, the protons are conducted to the cathode compartment by a PEM. Finally, in the cathode compartment, the protons are reduced to generate H_2 at high pressure, thus improving the specific volumetric energy density of the storage [1].

This pressurized hydrogen has a storage limit dictated by the balance of the following membrane properties: first, the force exerted by the pressurized hydrogen in the cathode compartment, where the membrane mechanical properties have their effect; second, the membrane permeability, i.e. the resistance of hydrogen to return to its molecular form; and third, the proton conductivity of the membrane, which dictates the maximum rate of proton transport protons, compensating in this way for any hydrogen loss by leakage [1,2]. An important weak point of the EHP system is the membrane on which storage efficiency will depend. In this sense, the DuPont Nafion® membrane based on perfluorosulfonic acid is

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widely used due to its excellent proton conductivity and its high chemical stability, as long as the membrane operates at 100% RH. Another alternative used as a solid electrolyte is the sulfonated poly (ether-ether ketone) (SPEEK), which is an aromatic polymer that offers thermal stability, proton conductivity comparable to Nafion® (depending on the sulfonation degree, SD) or even better, a low permeability (due to their channels being narrower) and greater mechanical stability [3].

The proton exchange membranes have some limitations such as low mechanical resistance, limited operations at low temperatures, high hydrogen crossover and, in particular SPEEK-based membranes with low proton conductivity. To overcome these limitations several hybrid membranes or organic/inorganic composite membranes have been the focus of research for researchers [4]. For the composite membranes synthesis, it is possible to improve the properties with a strict choice of materials. For example, at high temperatures, the membrane is dehydrated due to water evaporation. The proton transport will be limited if there is not an adequate amount of water, so the authors added some inorganic compound that allows the retention of water inside the polymer matrix. In recent advanced, examples of these compounds are SiO_2, ZrO_2, TiO_2 [5,6] or some clays such as Halloysite nanotubes (HNT) [7], which keep the membranes hydrated at relatively high temperatures (between 90 °C and 120 °C). As discussed above, an equally important property for EHP is the transport rate of H^+, which is directly related to proton conductivity. Although Halloysite nanotubes improve the mechanical properties of the membrane, they do not greatly improve the proton conductivity. For this reason, some authors have tested heteropolyacids such as phosphotungstic acid ($H_3PW_{12}O_{40} \bullet nH_2O$, PWA) in membranes based on SPEEK, considerably improving the proton conductivity of the membrane [8]. Therefore, in this work, composite membranes consisting of SPEEK/PWA-HNT loaded at 30% with respect to PWA and 15% with respect to HNTs were characterized by spectroscopic and electrochemical techniques.

2. Experimental methodology

2.1. Synthesis of membranes

2.1.1. Synthesis of SPEEK

The synthesized polymer was prepared from PEEK [Poly (Ether-Ether Ketone) from Victrex 450P, MW = 38 300] with a sulfonation reaction as follows: sulfonation is an electrophilic substitution reaction carried out by dissolving 5 g of PEEK in 100 mL of H_2SO_4 (Aldrich, 98%). The solution was stirred vigorously with a magnetic stirrer at T = 50 °C for several different periods of time to obtain different degrees of sulfonation. The reaction is stopped by precipitating the polymer in cold deionized water (T ≈ 4 °C). Subsequently, the excess acid was removed by washing with deionized water to pH ≥ 7. Then, the water was removed at T = 70 °C for t = 12 h followed by additional thermal processing at T = 120 °C for t = 2 h to stabilize the polymer [9]. The sulfonation degree (SD) was determined by titration [10].

2.1.2. HNT impregnated with PWA

The HNTs were impregnated with PWA (wt%/wt% 7: 3 respectively). The HNTs were dried for t = 24 h at T = 80 °C; then, an appropriate number of nanotubes was taken for dispersion in a water/PWA mixture at room temperature for t = 1 h, followed by a slow evaporation at T = 50 °C [11].

2.1.3. Membrane preparation

According to references, to increase the performance of membranes synthesized from SPEEK, the optimal concentration of the HNTs is 15% (wt/wt). For this reason, all the membranes were prepared at this percentage [12]. The polymer was dissolved in dimethylacetamide (DMAc) until a homogeneous solution was obtained. In contrast, the HNTs or fillers were dispersed in DMAc by ultrasound at room temperature. Subsequently, the fillers were added to the polymer solution and homogenized by magnetic stirring at T = 80 °C. When an appropriate viscosity was obtained, the membrane was obtained by the Doctor blade method [5].

2.2. Characterization of composite membranes and fillers

2.2.1. Physicochemical characterization of inorganic fillers

The fillers prepared were characterized by X-ray powder diffraction (XRD) analysis performed using a Philips X-ray automated diffractometer (model PW3710) with CuKα_1 radiation in the range $5° < 2\theta < 100°$. The morphology and microstructure of the HNTs and HNTs impregnated with PWA fillers were investigated by scanning electron microscopy (SEM using a JEOL model JSM-6060 LV microscope) and surface mapped with energy-dispersive spectroscopy (EDS, Bruker XFlash® 6110 detector).

2.2.2. Characterization of composite membranes

2.2.2.1. Physicochemical methods. The thermogravimetric analysis (TGA) was carried out with a 2950 TGA HR V5.5 TA in air, following the variation in the percentage weight loss, performed between 25 °C and 600 °C with a heating rate of 5 °C min^{-1} with the incorporation of a DSC. The morphologies of the composite membranes modified with HNT and HNT impregnated with PWA fillers were investigated by scanning electron microscopy (SEM using a JEOL model JSM-6060 LV microscope). The XRD analysis was performed similarly to the analyses employed on the inorganic fillers as mentioned in Section 2.2.1.

2.2.3. Mechanical characterizations

Membrane samples were equilibrated at 25 °C and 20% HR for 5 days before being cut into the dog-bone specimen shape for the tensile tests. A CMT4104 electrical tensile tester (SANS, Shernzhen, China) was used to measure the stress-strain behaviour of the sample at 25 °C and 20% RH with a strain rate of 2 mm min^{-1}, according to ASTM D882. At least five specimens were tested to determine the average value.

2.2.4. Water uptake (W_{Up}), Area swelling (AS), and Volume swelling (VS)

The measurements were performed in triplicate in order to avoid measurement errors in the experiments. The value of W_{Up} was calculated by the difference between the wet mass and dry mass of the samples. The methodology used to perform the tests is detailed by A. Saccà et al. [5]. All samples were evaluated from T = room temperature to 80 °C. The samples evaluated at T = room temperature were maintained for t = 24 h immersed in water, while the membranes evaluated at T = 50, 60, 70 and 80 °C were immersed in water for t = 2 h. The following formula was used to calculate the W_{Up} [13]:

$$W_{Up}(\%) = \left|\frac{m_{wet} - m_{dry}}{m_{dry}}\right| * 100 \quad (1)$$

where $\boldsymbol{m_{wet}}$ and $\boldsymbol{m_{dry}}$ represent the wet mass and dry mass, respectively. Swelling (Area and Volume, ΔA and ΔV, respectively) were evaluated by equations [6,14]: