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Synthesis and characterization of new membranes based on sulfonated polysulfone/Zn,Al-heptamolibdate LDH

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ABSTRACT

New proton conducting organic/inorganic nano hybrid polymer electrolyte membranes were synthe sized by solving casting method. Inorganic nanopowders were a layered double hydroxides (LDH) with Zn,Al cations in which heptamolybdate were inserted. These nanopowders were prepared by anion exchange method from hydrotalcite (LDH) with interlayer anions (NO_3). The sulfonated polymers were prepared by an electrophilic aromatic substitution reaction between the polymer and trimethylsylil cholorosulfonate (TMSCS).

The composites membranes were characterized by FTIR and TGA and water uptake was determined. Electrochemical impedance spectroscopy (EIS) was used to study the proton conductivity of the membranes. EIS measurements were performed facing the membrane to different HCl concentrations ($10^{-3} \leq c \leq 10^{-1}$ M). It was concluded that these new composite membranes present good thermal properties and proton conductivity slightly higher than SPSU.

1. Introduction

Perfluorinated polymers, such as Nafion, are the most widely used electrolyte in proton exchange membrane fuel cell (PEMFC) due to its high proton conductivity, excellent mechanical properties and good chemical and electrochemical stability. However, this type of membrane also exhibits some drawbacks, mainly the high cost, low stability at high temperatures, low conductivity at low humidity [1] or high temperature and high methanol crossover. For this reason, there are many efforts to find alternatives to these perfluorinated membranes [2,3].

Polysulfone (PSU) has attracted considerable interest due to its excellent thermal and mechanical stability, low cost and commercial availability. In particular, sulfonated polysulfone (SPSU) ionomer membranes have been extensively studied and tested for fuel cell applications [4,5]. In order to increase some properties of polymers, different inorganic fillers, such as, TiO_2 [6], ZrO_2 [7], phosphoanti monic acid [4], etc, were incorporated in SPSU.

Recently, we have prepared sulfonated polysulfone (SPSU)/layered double hydroxide (LDH) composite membranes, in which the con ductivity was improved [8]. Herein, we present the synthesis and characterization of new SPSU composites membranes with nanopow ders of Zn,Al LDH intercalated with a heptamolibdate, $(NH_4)_6Mo_7O_{24}$. The heteropolyacid, which is a strong Brönsted type acid, will minimize the basic properties of LDH and will provide higher proton mobility in the composite membrane.

2. Experimental section

Firstly, the sulfonation process was carried out in anhydrous conditions under N_2 following the method described by Chao et al. [9]. The solution of polysulfone (PSU) in 1,2 dichloroethane was treated with trimethylsilyl chlorosulfonate, $Si(CH_3)_3SO_3Cl$ (TMSCS) diluted in 1,2 dichloroethane($C_2H_4Cl_2$, DCE) and was maintained under magnetic stirring during 24 h at room temperature. Once the reaction was over, the sulfonated polymer was purified until neutral pH. Finally, the obtained polymer was dried at room temperature. The molar ratio of PSU: TMSCS was 1:3 and the sulfonation degree determined from ^1H NMR experiments was 0.77.

The synthesis of Zn,Al NO_3 (LDH) was carried out by the co precipitation method [8,10]. Thus, the solution of with Zn:Al molar ratio of 2, prepared with $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$, were added drop wise to a solution of 1 M NaOH, with stirring and the pH was maintained at 8.0. Afterward, intercalation of $(NH_4)_6Mo_7O_{24}$ were performed following Ref. [11]. The solution of $(NH_4)_6Mo_7O_{24}$ (1.1 g of $(NH_4)_6Mo_7O_{24}$ in 50 ml of decarbonated water) was added drop wise to the LDH solution (1 g of LDH in 150 ml of decarbonated water) under N_2 atmosphere and a constant 4.5 pH. The reaction mixture was stirred for a 24 h at 60 °C. The intercalation reaction was confirmed by XRD. The particle size of the powder is highly agglomerated as observed by

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SEM. The crystalline size determined by XRD using Scherrer equation and peak (0 0 2) was 7.9 nm.

Finally, membrane preparation was carried out. In this last step, dried sulfonated PSU was dissolved (5 wt%) in DMAc. Afterward, the HMo LDH particles were suspended in the polymer solution during 3 h with mechanical stirring and 1 h in an ultrasonic bath. Finally the solutions were cast on Petri glass dish and dried in the oven at 60 °C for 48 h and at 120 °C for 24 h. The obtained membranes were immersed in water to eliminate possible traces of solvent and, then, dried at room temperature. The amount of HMo LDH in the composite membrane was from 1 to 5 wt%. The thickness of membranes was around 100 μm.

Once prepared the membrane, a fully characterization of the films were carried out. Infrared spectra were recorded with a Perkin Elmer Spectrum GX FTIR spectrometer in the 4000 400 cm^{-1} range. Thermal characterization of membranes was performed by thermo gravimetric analysis (Perkin Elmer Pyris TGA1). The analyses were performed between 50 and 900 °C at a heating rate of 10 °C/min under air flow. Water uptake of all composite membrane samples was determined at room temperature, by immersion in deionized water during 72 h, using Eq. (1):

$$Water\ uptake = ((W_{wet} - W_{dry})/W_{dry}) \times 100 \qquad (1)$$

W_{wet} and W_{dry} correspond to the weights of membranes in wet and dry state, respectively.

The proton conductivity measurements were performed in a liquid test cell constituted by two half cells using ac impedance technique. The membrane was sandwiched between two o rings. A conventional electrochemical setup of four electrodes was used for these measurements involving two saturated Ag/AgCl electrodes (reference electrodes) and two graphite electrodes (secondary electrodes). The measurements were conducted at room temperature in an impedance/gain phase analyser (Solartron 1260) and an electrochemical interface (Solartron 1287). The frequency range was 1 MHz 10 Hz. Six different HCl solutions ($10^{-3} \leq c \leq 0.1$ M) were tested.

3. Results and discussion

FT IR analysis: Sulfonation process of the polysulfone was qualitatively confirmed by FTIR. The results indicated clearly the presence of sulfonic groups in the polymer backbone after sulfonation reaction (Fig. 1). In the frequency range of 1050 1000 cm^{-1} two characteristic peaks were observed [6]. In particular, the band located at 1014 cm^{-1} was assigned to the symmetric stretching vibration of the diphenylether unit, while the peak at 1028 cm^{-1} is due to the symmetric stretching vibration of the sulfonated group [12]. In the case of composite membranes, this characteristic shoulder of SPSU at 1028 cm^{-1} is slightly shifted to higher values
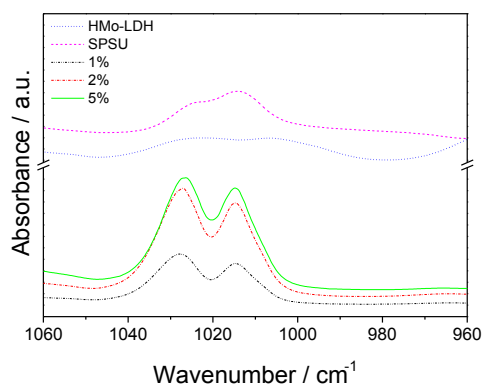
of wavenumber when inorganic filler increase, indicating weak interactions between the hydroxyl HMo LDH layer and the sulfonic group, probably due to hydrogen bonding. Furthermore, the intensity of this shoulder increased with the content of HMo LDH, indicating remarkable interaction between the HMo LDH and the SPSU.

Thermogravimetric analysis (TGA): The thermal stability of SPSU and composite membranes was studied by TGA (Fig. 2). SPSU membranes exhibited three weight losses: (i) between 50 and 250 °C corresponds to absorbed water bonded to sulfonic groups, (ii) between 250 and 450 °C, attributed to the desulfonation process and (iii) above 450 °C related to the main chain decomposition [13].

TGA curves of HMo LDH powder present two weight losses: between 50 and 175 °C corresponds to adsorbed water and the second one (175 400 °C) was attributed to the dehydroxilation of HMo LDH [11]. The presence of HMo LDH modifies slightly the thermal stability of the membranes. In all the cases, the desulfonation and main chain decompositions are delayed with the presence of the HMo LDH. The degradation of the main chain of the polymer (above 450 °C) depends on the amount of HMo LDH, being fully degraded at temperature less than 750 °C for membranes with 1 and 2% of HMo LDH and in the case of the sample with 5%, the degradation is similar to that of SPSU alone.

Water uptake: The water uptake at room temperature of membranes with different percentages of HMo LDH was evaluated. The amounts of absorbed water decreased as the HMo LDH increases (Fig. 3, right axis). These results are in agreement with the TGA analysis in the low temperature range (50 175 °C). This behavior was found in other composite membrane system [14] and it was attributed to the reduction of the free volume and swelling ability.
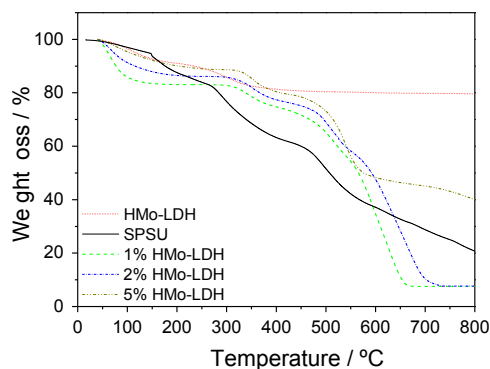

Fig. 2. Thermogravimetric analysis of HMo-LDH, SPSU and their respective HMo-LDH composites.
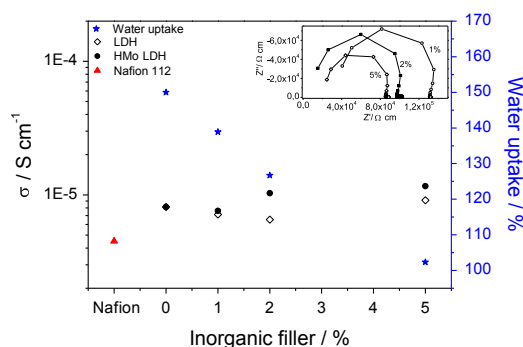

Fig. 3. Water uptake (★) and conductivity of SPSU/HMo-LDH hybrid composite membranes with the inorganic filler. In the inset the Nyquist plots are plotted. Values are also compared with nanocomposites of SPSU/LDH [8].

Fig. 1. FTIR spectra of SPSU, HMo-LDH and SPSU with 1,2,5% of HMo-LDH.

Proton conductivity: The proton conductivity was performed using electrochemical impedance spectroscopy (EIS). All mem branes were placed in contact with different acid concentrations ($10^{-3} \leq c \leq 0.1$ M) during a specific period of time. As expected Nyquist plots changed with the HCl concentration (data do not shown) and it was attributed to the concentration dependence of the electrolyte solution embedded in the membrane matrix [8,15].

The evolution of the conductivity with the amount of HMo LDH is showed in Fig. 3, left axis. This value was obtained from the intercept on the real axis at the high frequency end of the Nyquist plot (inset of Fig. 3). The conductivity values increases with the amount of HMo LDH and it is slightly higher than nanocomposites membranes of SPSU/LDH [8].

4. Conclusions

A new class of organic/inorganic nano hybrid polymer electrolyte membranes based on sulfonated polysulfone and heptamolybdate inserted in layered double hydroxide nanocomposite membranes were prepared.

The presence of HMo LDH in the membranes was confirmed by FTIR. The introduction of HMo LDH improved the thermal beha viour. The conductivity of composite membranes is in the same range of the SPSU and slightly increases with the inorganic filler. These results indicated that HMo LDH/SPSU nanocomposites mem branes are very promising for being applied as proton exchange membranes.

Acknowledgements

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