Synthesis and characterisation of proton conducting styrene-co-methacrylate–silica sol–gel membranes containing tungstophosphoric acid

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Abstract

The increase of the operation temperature in proton exchange membrane fuel cell (PEMFC) above 100 °C is a great concern for the application of this type of cells in electric vehicles. Hybrid organic–inorganic membranes with nanosized interfaces can combine the main properties to meet this objective. Poly (styrene-co-methacrylate)–silica covalent hybrid membranes have been synthesised by copolymerization of monomers (styrene (STY) and 2-hydroxyethyl methacrylate (HEMA)), with formation of covalent bonds between hydroxyl group from the latter and pre-hydrolyzed tetraethoxysilane. Tungstophosphoric acid hydrate was incorporated to endow the membranes of proton conductivity. The optimal composition and synthesis conditions to promote organic polymerization and sol–gel condensation avoiding phase separation are important issues of this work. The structural analysis shows homogeneous membranes without phase separation. The combination of water uptake and water retention properties provided by SiO₂ and tungstophosphoric acid leads to high proton conductivity (maximum values around 1 S/cm) at 120 °C.

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Keywords: PEMFC; Hybrid conductor; Heteropoly acid salts; Sol–gel technique; Proton conductivity

1. Introduction

There is a great interest in proton exchange membrane fuel cells (PEMFC) for different applications, especially for transportation [1]. The major limitations of actual PEMFCs that use polymeric “Nafion” type membranes are CO poisoning of Pt anode electrocatalysts, a complex water management, and problems associated with the use of hydrogen as fuel (fabrication, storage and safety). These kind of membranes limit the operation temperature of the cell to temperatures as low as 80 °C. If the membranes were capable of operation at temperatures above 100 °C without substantial humidification, the CO poisoning would be reduced, and it would also alleviate the water management problems in PEMFCs. Moreover, the increase of PEMFC operation temperature would allow increased fuel cell reaction kinetics, lower consumption of platinum catalyst, and direct use of low-temperature fuels such as methanol. However, water and methanol crossover remarkably increases with temperature, reducing the fuel cell efficiency [2,3].

Nano-ordered composite materials consisting of organic polymers and inorganic components have been attracting attention for their use in new high-performance materials. One interesting alternative to polymeric membranes in order to reach higher fuel cell operation temperature is the hybrid organic–inorganic membranes with nanosized phases and interfaces. The inorganic component allows the thermal stability to be increased and combines it with the mechanical and proton conductivity properties of the organic component. Similarly, the inorganic phase can improve chemical stability and high temperature proton conductivity of the membranes by the increase of water retention up to
higher temperatures [4,5]. One of the research fields in hybrid organic–inorganic materials is based on the reaction between monomers and silicon alkoxides to form covalent bonds that permit the preparation of nanostructured interfaces. To reach this goal, the monomers have to contain OH groups that react with the M–OH groups of pre-hydrolyzed metallic alkoxides in suitable conditions [6–9].

The membrane conductivity is proportional to the concentration of the mobile protons within the membrane. Thus, in this context, a possible way to increase the proton conductivity is to dope the hybrid membrane with an appropriate acidic solid, melt or solution of low volatility that increases the proton concentration via proton-transfer reactions in the same way as water does, but in the absence of substantial quantities of water [10]. The acidity of the solutions of heteropoly acids (HPAs) is reflected on their proton conductivity which is of the same order of magnitude as that of ordinary mineral acids. HPAs also show high proton conductivity which is of the same order of magnitude solutions of heteropoly acids (HPAs) is reflected on their reactions in the same way as water does, but in the absence of an appropriate acidic solid, melt or solution of low volatility.

The aim of this work has been the synthesis and characterisation of tungstophosphoric acid doped poly(styrene-co-methacrylate)–silica covalent hybrid membranes. The experimental procedure includes copolymerization of two monomers: styrene and 2-hydroxyethyl methacrylate, and hydrolysis–polycondensation of tetraethyl orthosilicate. Tungstophosphoric acid hydrate was incorporated to endow the membranes of proton conductivity. The optimal composition and synthesis conditions to promote organic polymerization and sol–gel condensation, avoiding phase separation, is an important issue of this work. TGA-DTA, XRD, FTIR, FE-SEM and EIS have been used for characterising the obtained membranes.

2. Experimental

Tetraethyl orthosilicate (TEOS) from ABCR, tungstophosphoric acid hydrate (PWA) from MERCK, styrene (STY) and 2-hydroxyethyl methacrylate (HEMA) both from ALDRICH were used as precursors. Four different compositions were produced with 10 and 25 molar % of SiO₂, and 3 and 15 wt.% of PWA for each silica content. In all cases, the organic component was prepared using equimolar amounts of STY and HEMA. Sols were prepared by mixing two solutions. Solution A was prepared by dissolving PWA in water (molar ratio of H₂O/TEOS=3.5 and 7.0 for 3 and 15 wt.% of PWA, respectively) and absolute ethanol, stirring at room temperature for 10 and 15 min. In this synthetic procedure, acid was not placed at 55°C. Two solutions were mixed and stirred at room temperature for 30 min. Solution B was prepared by stirring at room temperature for 30 min STY, HEMA and 1,1’-azobis(cyclohexanecarbonitrile) from ALDRICH in 0.5 wt.% with respect of STY+HEMA as initiator of the free-radical copolymerization. Then, TEOS was added with an additional stirring at room temperature for 30 min. Both solutions were mixed and stirred at room temperature for another 15 min. In this synthetic procedure, acid was not intentionally added because PWA acts as an acidic catalyst besides donating protonic carriers for conduction. The sols were cast in glass and polytetrafluoroethylene moulds and placed at 55°C to initiate the free radical co-polymerization of STY and HEMA, and continue the sol–gel reactions to produce solid materials after 24 h. The so obtained hybrid membranes were further treated at 150°C during 24 h to complete drying and curing.

The fracture surfaces of the hybrid membranes were examined on a HITACHI S-4700 field emission scanning electron microscope (FE-SEM). The thermal behavior (TGA-DTA) of samples treated at 150°C was followed using a Netzsch STA 409 with a heating rate of 10°C/min in air up to 900°C. X-ray diffraction (XRD) was performed using a Siemens Model D5000 on samples heat-treated at 150°C. Fourier transform infrared (FTIR) spectra were recorded using a Perkin-Elmer 1760X in the frequency range 400–4000 cm⁻¹ using KBr pellets, and using a drop of about 1 μl between two KRS-5 window crystals to analyze HEMA.
The conductivity of hybrid membranes treated at 150 °C was obtained by Electrochemical Impedance Spectroscopy (EIS) using a HEWLETT PACKARD 4192A impedance analyzer and Pt electrodes of about 0.5-mm diameter. The measurements were conducted as a function of both relative humidity (RH) and temperature. The samples were allowed to equilibrate at the desired RH for 24 h inside a sealed chamber containing saturated solutions of salts: Ca(N2O3)2·4H2O for the 33–53% range, NaNO3 for the 64–75% range, KNO3 for the 80–92% range, and water vapor for the 100% [18]. The frequency was varied from 10 Hz to 10 MHz, and the EIS curves were resolved using Equivalent Circuit version 3.97 software (IBM-CGA screen).

3. Results and discussion

All the hybrid membranes, with a thickness around 200 μm, are homogeneous, highly transparent and yellow coloured after the polymerization process at 55 °C. The thermal treatment at different temperatures up to 150 °C turns the membrane colour to brown without losing transparency. The high homogeneity of the hybrid membranes indicates no phase separation suggesting that the organic and inorganic components were blended at molecular level through formation of covalent bonds between hydroxyl group from HEMA and pre-hydrolyzed tetraethoxysilane. Fig. 1 shows FE-SEM photographs at different magnifications of a fracture surface of a hybrid membrane with 25% SiO2 and 15% PWA treated at 150 °C. The figures present a homogeneous material formed by nanosized agglomerates without phase separation. It is possible to observe low size porosity (~10 nm), very important to reach adequate proton conductivity because of its high water retention capability.

TGA curves of hybrid membranes with different percentages of SiO2 and PWA are shown in Fig. 2. These curves can be divided in regions corresponding to different weight loss ranges. A first region, between room temperature and 200 °C, shows a slight weight loss attributed to desorption of physically absorbed water and residual solvents. The value is relatively low because the membrane was previously treated at 150 °C. In this region, the slightly higher mass loss in samples with 15% PWA could be due to the release of structural water from lower PWA hydrates containing six water molecules [12,16]. The second region in TGA curves, between 200 and 400 °C, presents an important weight loss assigned to the release of more structural water from PWA and solvents and water generated during the sol–gel reactions at temperatures close to 200 °C.

![Fig. 1. FE-SEM photographs of fractured surface of the hybrid membrane with 25% SiO2 and 15% PWA treated at 150 °C.](image1.jpg)

![Fig. 2. TGA-DTA curves of hybrid membranes with different percentages of SiO2 and PWA.](image2.png)
and to the partial thermal decomposition of the polymeric network at temperatures between 300 and 400 °C. Two small endothermic peaks at around 160 and 250 °C agree with the loss of different structural water from PWA [11,12], and an intense exothermic peak centered at around 340 °C corresponds to the partial combustion of the polymeric component. The weight loss rates in this second region are higher for samples with 3% PWA because of its higher percentage of organic component. In the third region, above 400 °C, the weight loss rates are lower but continuous up to 750 °C. The tendency is similar in all the samples, and this weight loss is assigned to the final thermal decomposition of polymeric network and structure collapse of PWA with loss of phosphorus. The broad exothermic peak between 400 and 800 °C observed in the DTA curve agrees with this continuous weight loss. The small weight loss observed at low temperatures and the position of the lower temperature exothermic peak, centered at 340 °C, indicate that the thermal stability of these hybrid membranes is quite sufficient and will be stable enough within temperature range of PEMFC application.

XRD patterns of membranes treated at 150 °C only show the typical amorphous broad peak at 2θ values around 20° characteristic of silicate gels, and a very broad peak at about 25° only in samples with 15% PWA. No defined diffraction peak characteristic for PWA appears, and only the broad peak observed at 25° can be related with PWA in the hybrid membrane without formation of crystallites. This behavior also suggests that PWA interacts with hydroxyl groups from HEMA and silanols from hydrolyzed TEOS through coulombic interaction and hydrogen bridges [11,19].

FTIR transmission spectra of the pure PWA, pure HEMA and hybrid membranes with different percentages of SiO₂ and PWA are shown in Fig. 3. Assignments of the main bands (Table 1) are based on the literature values [11,13,20-23]. The bands present in the hybrid membranes are in good agreement with all the bands representing Keggin units of PWA, indicating the preservation of Keggin ions geometry inside the hybrid structure. As the PWA content in the sample increases, the intensities of their characteristic bands rise. The corner-sharing W–Oₓ c–W band at 800 cm⁻¹ in pure PWA is shifted to values around 815 cm⁻¹ when PWA is inside the membrane structure. This behavior can be explained by the adequate separation among Keggin units and a vibration less disturbed by anion–anion interactions [23]. On the other hand, there is a small shift of edge-sharing W–Oₓ b–W band from 885 cm⁻¹ in pure PWA to 895 cm⁻¹ in the samples with PWA supported on hybrid membranes. The frequency shift of about 10 cm⁻¹ could indicate that the Keggin unit of PWA interacts with hydroxyl groups of silanols and HEMA [11]. The PWA clusters are probably stabilized in the membrane through a

<table>
<thead>
<tr>
<th>Vibration frequency (cm⁻¹)</th>
<th>Bond assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>Si–O–Si bending</td>
</tr>
<tr>
<td>700, 760</td>
<td>Aromatic ring</td>
</tr>
<tr>
<td>815</td>
<td>Corner-sharing W–Oₓ c–W</td>
</tr>
<tr>
<td>895</td>
<td>Edge-sharing W–Oₓ b–W</td>
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<tr>
<td>980</td>
<td>Terminal W–Oₓ d–W</td>
</tr>
<tr>
<td>1080</td>
<td>Si–O–Si, C–O–C, P–Oₓ</td>
</tr>
<tr>
<td>2935, 1170</td>
<td>Methacrylate</td>
</tr>
<tr>
<td>1600, 1495, 1455, 1385</td>
<td>Aromatic ring</td>
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<tr>
<td>1635</td>
<td>C=O bond</td>
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<tr>
<td>1725</td>
<td>C=O bond</td>
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<tr>
<td>2860</td>
<td>O–H stretching</td>
</tr>
<tr>
<td>3250–3650</td>
<td>OH groups</td>
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Fig. 3. FT-IR spectra of pure PWA, pure HEMA and hybrid membranes with different percentages of SiO₂ and PWA.
coulombic interaction and hydrogen bridges with the inorganic component, mainly by Si–OH groups [16]. The important presence of hydroxyl groups in the high frequency range confirms the capability of hydrogen bond formation, essential in proton conducting materials working with water as the “vehicle” for proton transport. An increase of inorganic component (SiO$_2$ and PWA) leads to less intense peaks related with the aromatic ring [23].

All the complex impedance spectra (Nyquist plot) obtained at low temperature and low RH present a semicircle through the origin at high frequencies and inclined lines at low frequencies. As an example, Fig. 4 shows the Nyquist plots of the membrane with 15% PWA and 25% SiO$_2$ at different temperatures in the 64–75% RH range. The semicircle represents a typical equivalent circuit of a resistor and a capacitor connected in parallel corresponding to the bulk electrical properties, and the line a Warburg impedance caused by the diffusion process of protons. The conductivity $\sigma$ of the samples in the transverse direction was calculated from the impedance data, using the relation $\sigma = t/RS$. In this equation, $t$ and $S$ are the thickness and electrode area of the sample, respectively. $R$ was obtained from the intersect of the semicircle with the Re $Z$ axis calculated using the Equivalent Circuit 3.97 software.

Fig. 5 shows an example of Nyquist plot obtained from samples measured at high temperature and high RH. In this case, the lower resistance lead to spectra that only present the inclined lines and, sometimes, a part of the semicircle at higher frequencies.

The membranes with 3% PWA behave like insulators with conductivity values around $10^{-9}$ S/cm. The increase of PWA content leads to a significant rise of proton conductivity. Fig. 6 presents a 3D plot of conductivity values as a function of temperature and relative humidity of a membrane with 10% SiO$_2$ and 15% PWA. The general trend observed is the increase of the conductivity with both relative humidity and temperature up to 120–130 $^\circ$C. Although the relative humidity decreases with temperature for a specific salt, the conductivity increases with the temperature for the three salts used. Otherwise, the proton conductivity was found to be quite dependent on humidity. Relative humidity influences the amount of water which occupies the reticular positions in the structure of PWA and
also the amount of water adsorbed on the silica. Both of these enhance the transport of protons through the material. On the other hand, because the hybrid membrane comprises SiO$_2$ and PWA as a part of the structure, the materials can be high temperature tolerant proton conducting membranes. The samples measured at 100% RH show a rise of conductivity with temperature up to 120–130 °C due to the water retention capability of SiO$_2$ and PWA, and then decreases with a loss of conductivity in two orders of magnitude up to 160 °C.

Fig. 7 is an Arrhenius plot of the proton conductivity as a function of temperature at different relative humidity ranges for the 10% SiO$_2$–15% PWA membrane. As observed in this figure, the improvement of conductivity with the relative humidity is significant. The increase of conductivity with temperature, broken at about 120–130 °C, suggests the presence of two competing trends, one enhancing and the other reducing conductivity. As proton conductivity is in general thermally stimulated, it is reasonable to expect a rise in conductivity with temperature. The decay in the conductivity values above 120–130 °C suggests that dehydration of the membrane occurs. Thus, it is very important not only the capacity of water uptake but moreover the capacity of the membrane to retain water at higher temperatures. The incorporation of SiO$_2$ improves both water uptake and water retention at high temperature of the hybrid membrane increasing the high temperature stability of the proton conductivity. A similar trend is observed with Nafion membranes. The modification of these membranes with sol–gel oxides based on SiO$_2$ has shown a significant improvement in fuel-cell tests. The cell potentials and current densities at 130 °C are greater than that obtained with unmodified Nafion at 80 °C [4,5]. An Arrhenius-type dependency of conductivity on temperature (Fig. 7) is clear for all relative humidity ranges below 120 °C. The activation energies for proton conduction are 27, 19 and 11 kJ/mol for the 33–52%, 65–75% and 82–92% RH, respectively. These results suggest a common charge transfer mechanism based on the Grotthus reorientational proton transfer scheme [24]. In this mechanism, the activation energy for proton conduction is about 10–40 kJ/mol [25]. The values obtained decrease when relative humidity increases. This behavior is related with the concentration of water because these molecules are the “vehicles” for the...
transfer of protons as \( H_2O^- \). At higher RH water molecules are closer, reducing the activation energy for the proton transfer.

Fig. 8 shows a 3D plot of conductivity values as a function of temperature and relative humidity of the membrane with 25% SiO\(_2\) and 15% PWA. The trend of conductivity values is similar to that observed with the membrane containing 10% SiO\(_2\), i.e. increase of conductivity with temperature and relative humidity up to 120–130 °C, and a further decrease at higher temperatures. The main difference between both membranes is that conductivity values are three orders of magnitude higher for membranes with 25% SiO\(_2\). This significant rise of conductivity can only be associated with the higher percentage of silica in this membrane. The amount of PWA was fixed at 15% in order to obtain mechanically stable membranes because the incorporation of PWA leads to an increase of fragility. On the other hand, 15% of PWA is not enough to provide sufficient water molecules and an important amount of SiO\(_2\) is necessary (25% in this case) to prepare high proton conducting membranes.

Proton conductivity is quite dependent on the humidity in this membrane. For example, for a temperature fixed at 50 °C, the conductivity changes from \( 4.6 \times 10^{-4} \) S/cm with 39% RH to \( 6.2 \times 10^{-1} \) S/cm with 87% RH. The high conductivity values obtained at 120–130 °C are an important improvement to the development of high temperature proton conducting membranes, and indicates a strong interaction between water and hybrid membrane.

The Arrhenius plot at different relative humidity ranges of the membrane with 25% SiO\(_2\) and 15% PWA (Fig. 9) shows the same trend observed with the membranes containing 10% SiO\(_2\). The Arrhenius-type dependency is also clear in this figure. The activation energy for proton conduction is 29, 27 and 11 kJ/mol for the 33–53%, 64–75% and 80–91% RH, respectively. The values are similar to those obtained with the membrane of 10% SiO\(_2\) showing that the mechanism of proton transfer is the same in both cases.

Summarising, the combination of water uptake and water retention properties provided by SiO\(_2\) and PWA leads to high proton conductivity up to 120–130 °C. On the other hand, it is necessary to have an enough amount of SiO\(_2\) and PWA in order to produce an adequate path for proton conduction. An increase of temperature above 120–130 °C
originates a decay in conductivity, suggesting that dehydration of the membrane occurs. The use of pressure should lead to a reduction of dehydration permitting an increase of the operation temperature above 130 °C. Further work is in progress in order to evaluate the performance and stability of these membranes in fuel cell tests, and to determine their gas permeation properties.

4. Conclusions

Poly (styrene-co-methacrylate)–silica covalent hybrid membranes have been synthesised by copolymerization of monomers (styrene and 2-hydroxyethyl methacrylate), with formation of covalent bonds between hydroxyl group from the latter and pre-hydrolyzed tetraethoxysilane. Tungstophosphoric acid hydrate was incorporated to endow the membranes of proton conductivity. FE-SEM shows a homogeneous membrane without phase separation, and thermal analysis indicates a thermal stability close to 300 °C. Structural analysis by XRD and FT-IR suggests that tungstophosphoric acid interacts with SiO₂ and hydroxyl groups from 2-hydroxyethyl methacrylate through an acid–base reaction. The combination of water uptake and water retention properties provided by SiO₂ and tungstophosphoric acid leads to high proton conductivity (maximum values around 1 S/cm) at 120–130 °C. It is necessary to have an enough amount of SiO₂ and tungstophosphoric acid in order to produce an adequate path for proton conduction. A decay in conductivity was observed at higher temperatures, suggesting that dehydration of the membrane occurs.

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