

Short communication

Proton-conducting 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 nano-sized interfaces can combine the main properties to meet this objective. Methacrylate–silica covalent hybrid membranes have been synthesised by polymerization of 2-hydroxyethyl methacrylate and 3-methacryloxypropyl trimethoxysilane, and hydrolysis–polycondensation of alkoxide radicals. Tungstophosphoric acid hydrate was incorporated to endow the membranes with proton conductivity. The composition and synthesis conditions to promote organic polymerisation and sol–gel condensation avoiding phase separation have been optimised. The structural analysis shows homogeneous membranes without phase separation. The water retention properties provided by SiO₂ and tungstophosphoric acid leads to high proton conductivity (maximum values around $3 \times 10^{-2} \text{ S cm}^{-1}$) at 100–150 °C. A 0.5 M % of Tungstophosphoric acid (PWA) is enough to build well-connected paths for proton conduction.

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1. Introduction

A serious environmental issue today is the contribution to pollution from internal combustion engine vehicles. Compared to internal combustion engines, proton-exchange membrane fuel cells (PEMFC) in transportation operate with zero emissions of environmental pollutants [1,2]. Limitations of actual PEMFCs, that use Nafion™ membranes, are their poor water retention above 80 °C, CO poisoning of Pt anode electrocatalysts and problems associated with the use of hydrogen as fuel (fabrication, storage and safety). If the membranes were capable of operation at temperatures above 100 °C without substantial humidification, the CO poisoning would be reduced, given that the absolute free energy of adsorption of CO on Pt has a larger positive temperature dependence than that of H₂, meaning that the CO tolerance level increases [3], 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 and lower consumption of platinum catalyst [3,4]. On the other hand, further development of high temperature proton-exchange membranes is required in order to allow the practical use of direct methanol fuel cells (DMFC). These fuel cells take advantage of a safer fuel with a higher energy density per unit volume, compared to hydrogen-fed units. However, the slow oxidation kinetics of methanol at temperatures below 100 °C does not allow, at present, the use of DMFC units with efficiencies as high as those of PEMFC units. Consequently, improvements in the thermal stability of membranes are relevant to DMFC, as well as PEMFC [5].

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 nano-sized phases and interfaces. The inorganic component allows the thermal sta-

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bility 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 [6,7]. 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 nano-structured interfaces. To reach this goal, the monomers have to contain OH groups that react with the M–OH groups of pre-hydrolysed metallic alkoxides in suitable conditions [8–11].

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 [12]. Tungstophosphoric acid, $H_3[P(W_3O_{10})_4]$ (PWA), is a heteropolyacid (HPA) with high proton conductivity. The basic structural unit of PWA is the Keggin anion $(PW_{12}O_{40})^{3-}$ which consists of the central PO_4 tetrahedron surrounded by four W_3O_{13} sets linked together through oxygen atoms. Each W_3O_{13} set is formed by three edge-sharing WO_6 octahedra. They form channels which can contain up to 29 water molecules in different hydrate phases. This variety leads to different protonic species and hydrogen bonds of different strength [13,14]. The consequence is high proton conductivity at room temperature. Hydrated PWA is known to present values at around $0.18 S cm^{-1}$ [15,16]. Lower hydrates of PWA containing six water molecules are stable up to $180^\circ C$ [13], an important property to prepare PEMFC membranes working at temperatures higher than $100^\circ C$.

When appropriately incorporated, the hydrated PWA is expected to endow the membrane with its high proton conductivity. In spite of the promising initial results obtained using PWA in PEMFC, the cell leaked some dissolved acid and performance decayed. To overcome this problem, it would be interesting to investigate the possibility of blocking the PWA in the membrane. The processes of immobilisation by chemical attachment or entrapment are more convenient compare to physisorption [17]. The polyanion PWA clusters can be stabilized within the membrane through a strong coulombic interaction with an inorganic framework [18,19]. If the assembled PWA is nano-segregated, the strongly acidic phase originates an ionic conduction path with continuous channels. On the other hand, the presence of hygroscopic inorganic oxides inside the membrane enhances water retention at high temperatures extending the operation range [6,7] and reduces the methanol crossover effect in direct methanol fuel cell [20].

In this paper, we report the results on the synthesis and characterisation of tungstophosphoric acid doped methacrylate–silica covalent hybrid membranes. The experi-

mental procedure includes polymerization of 2-hydroxyethyl methacrylate (HEMA) and 3-methacryloxypropyl trimethoxysilane, and hydrolysis–polycondensation of alkoxide radicals. Tungstophosphoric acid hydrate was incorporated to endow the membranes of proton conductivity. The optimal composition and synthesis conditions to promote organic polymerisation and sol–gel condensation, avoiding phase separation, is an important issue of this work. TGA–DTA, FT-IR and EIS have been used for characterising the obtained membranes.

2. Experimental

Tungstophosphoric acid hydrate from Merck, 3-methacryloxypropyl trimethoxysilane (MPS) and 2-hydroxyethyl methacrylate both from Aldrich were used as precursors.

Eight different compositions were produced combining the precursors (Table 1). Sols 1 and 2 were prepared by mixing two solutions. Solution A was prepared by mixing absolute ethanol, calculated amounts of MPS and HCl 1N (molar ratio of water/MPS = 0.75) stirring at room temperature for 1 h. Solution B was prepared by stirring at room temperature for 30 min HEMA and 2,2'-azobis(isobutyronitrile) (AIBN) from Fluka in 0.5 wt% with respect of MPS + HEMA as initiator of the free-radical co-polymerization. Both solutions were mixed and stirred at room temperature for another 5 min. Then, H_2O (total molar ratio of water/MPS = 1.5) was added with an additional stirring at room temperature for 30 min. Sols 3–8 were prepared by mixing absolute ethanol, MPS and HEMA, stirring at room temperature for 15 min. PWA was incorporated and dissolved by stirring for 30 min, and finally, AIBN was dissolved also with stirring for another 30 min. In this synthetic procedure, water and acid were not intentionally added because PWA contains enough water molecules in its structure and acts as an acidic catalyst besides donating protonic carriers for conduction [19].

The sols were cast in glass and polytetrafluoroethylene moulds and placed at $60^\circ C$ to initiate the free-radical co-polymerisation of MPS and HEMA, and continue the sol–gel reactions to produce solid materials after 24 h. The so-obtained hybrid membranes were further treated at $150^\circ C$ during 24 h to complete drying and curing.

Table 1
List of hybrid membrane compositions (M %)

Sol number	HEMA	MPS	PWA
1	85	15	0
2	70	30	0
3	84.5	15	0.5
4	69.5	30	0.5
5	84	15	1.0
6	69	30	1.0
7	83.5	15	1.5
8	68.5	30	1.5

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⁻¹ in air up to 900 °C. FT-IR spectroscopy was used to study the free-radical polymerization of HEMA and MPS. A Perkin-Elmer model 1720X with a resolution of 2 cm⁻¹ and a frequency range of 4000–400 cm⁻¹ was used. Each spectrum was obtained by adding a drop of about 1 μl of solution between two KRS-5 window crystals by using a microburette. Each spectrum was obtained at different reaction times. The same spectrometer was used to analyze crushed samples using KBr pellets. The conductivity of hybrid membranes treated at 150 °C was obtained by electrochemical impedance spectroscopy (EIS) using a Hewlett-Packard 4192A impedance analyzer and Ag electrodes. 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 a saturated solution of NaNO₃ for the 64–75% range and water vapor for the 100% [21]. The frequency was varied from 10 Hz to 10 MHz and the EIS curves were resolved using equivalent circuit software [22].

3. Results and discussion

The hybrid membranes are homogeneous, highly transparent and yellow coloured after the polymerisation process at 60 °C. The thermal treatment at 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, and PWA is well dispersed in the structure.

Fig. 1 shows the FT-IR transmission spectra in the 1900–400 cm⁻¹ range of sol 8 at different times at 60 °C in order to study the free-radical co-polymerisation of MPS and

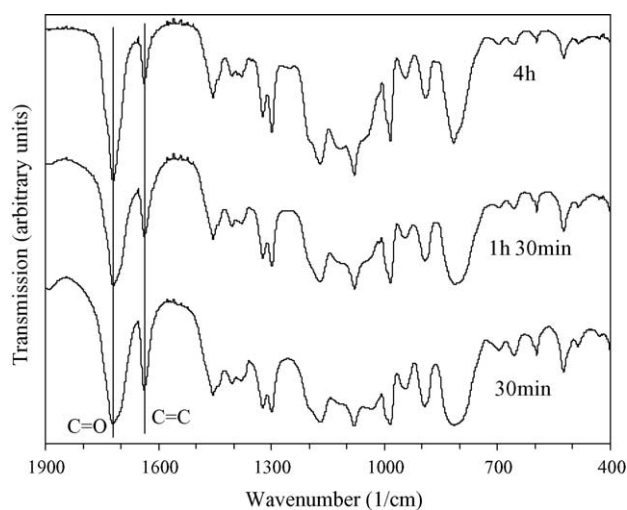


Fig. 1. FT-IR spectra of sol 8 (68.5HEMA–30MPS–1.5PWA) at different reaction times at 60 °C.

Table 2
Assignments of the main absorption bands

Vibration frequency (cm ⁻¹)	Bond assignment
528, 597	PWA bonds
820	Corner-sharing W–O _c –W
898	Edge-sharing W–O _b –W
986	Terminal W–O _d
1083	Si–O–Si, C–O–C, P–O _a
1180, 1301, 1325, 1457	Methacrylate bonds
1640	C=C bond
1725	C=O bond

HEMA. Assignments of the main bands (Table 2) are based on the literature values [8,11,14,17,23,24]. The bands present in the spectra are in good agreement with all the bands representing Keggin units of PWA, indicating the preservation of Keggin ions geometry inside the hybrid structure. The band at 1640 cm⁻¹, assigned to the C=C bond, presents a reduction of intensity with time showing that the polymerisation reaction proceeds fast. This reaction is almost complete after 24 h yielding a thin membrane. Others bands from methacrylate groups of HEMA and MPS do not change in the thermal treatment at 60 °C showing these bonds are stable in the process. The analysis of spectra corresponding to other sols presents a similar behaviour without presence of any influence of the PWA content.

FT-IR transmission spectra of pure PWA and 85HEMA–15MPS, 84HEMA–15MPS–1.0PWA and 83.5HEMA–15MPS–1.5PWA hybrid membranes treated at 150 °C are shown in Fig. 2. A small peak at 1640 cm⁻¹ assigned to C=C bond remains and its oxidation produces the change of color observed. Bands of methacrylate groups of HEMA and MPS do not show any change compared with the same bands in Fig. 1, showing these groups are stable in all the process. The bands of PWA present in the spectra indicate the preservation of Keggin ions geometry inside the hy-

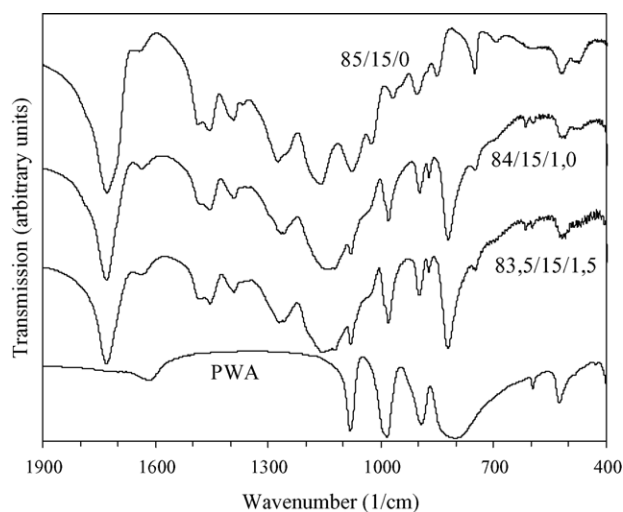


Fig. 2. FT-IR spectra of pure PWA and 85HEMA–15MPS, 84HEMA–15MPS–1.0PWA and 83.5HEMA–15MPS–1.5PWA hybrid membranes treated at 150 °C.

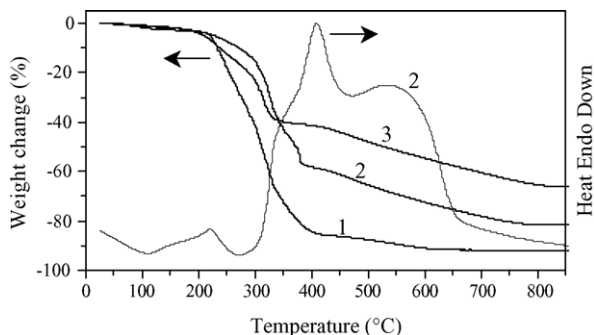


Fig. 3. TGA–DTA curves of hybrid membranes treated at 150 °C: (1) 85HEMA–15MPS, (2) 84.5HEMA–15MPS–0.5PWA and (3) 83.5HEMA–15MPS–1.5PWA.

brid structure. As the PWA content in the sample increases, the intensities of their characteristic bands rise. The broad corner-sharing $W-O_c-W$ band at 800 cm^{-1} in pure PWA is shifted to values around 817 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 [24]. On the other hand, there is a small shift of edge-sharing $W-O_b-W$ band from 885 cm^{-1} in pure PWA to 894 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 [17]. The PWA clusters are probably stabilized in the membrane through a Coulombic interaction and hydrogen bridges with the inorganic component, mainly by Si–OH groups [18,19].

TGA–ATD curves of 85HEMA–15MPS, 84.5HEMA–15MPS–0.5PWA and 83.5HEMA–15MPS–1.5PWA membranes are shown in Fig. 3. These curves can be divided in regions corresponding to different weight loss ranges. TGA curves show a slight weight loss (around 3%) between room temperature and 150 °C attributed to desorption of physically absorbed water and residual solvents. The value is relatively low because the membrane was previously treated at 150 °C. A small endothermic peak at 120 °C agrees with the loss of physically absorbed water. The second region in TGA curves, between 150 and 400 °C, presents an important weight loss assigned to the release of structural water from PWA [13,18] and solvents and water generated during the sol–gel reactions at temperatures close to 150 °C, and to the partial thermal decomposition of the polymeric network at temperatures between 300 and 400 °C. An endothermic peak at around 280 °C and an exothermic peak at around 360 °C agree with these weight variations. The weight loss in this second region is higher for samples without PWA (81%) because of its higher percentage of organic component. The same trend is observed on the samples with PWA, the membrane with less PWA shows a higher weight loss (55%) compared with the sample with more PWA (38%). In the third region, above 400 °C, the weight loss rates are lower but continuous up to 850 °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 exothermic peaks at 415 and 550 °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 360 °C, indicate that the thermal stability of these hybrid membranes are quite sufficient and will be stable enough within temperature range of PEMFC application.

All the complex impedance spectra (Nyquist plot) 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 84.5HEMA–15MPS–0.5PWA membrane at different temperatures. 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 σ of the samples in the transverse direction was calculated from the impedance data, using the relation $\sigma = t/RS$, where t and S are the thickness and electrode area of the sample, respectively. R was obtained from the intersection of the semicircle with the $\text{Re}(z)$ axis calculated using the equivalent circuit software. The increase of temperature leads to smaller semicircles (resistance reduction) because of proton conductivity is in general a thermally stimulated process.

Fig. 5 presents a plot of conductivity values as a function of temperature and relative humidity of the hybrid membranes with 0.5 M % PWA. The general trend observed is the increase of conductivity with temperature up to 100 °C, and similar conductivity values above this temperature. The behaviour of both membranes is similar, although a slightly

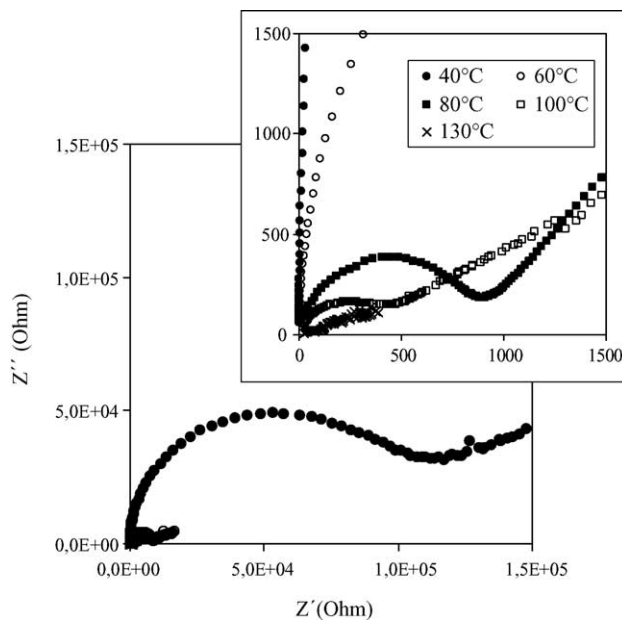


Fig. 4. Nyquist plots of the 84.5HEMA–15MPS–0.5PWA membrane at different temperatures. The high frequency region is shown in an expanded view.

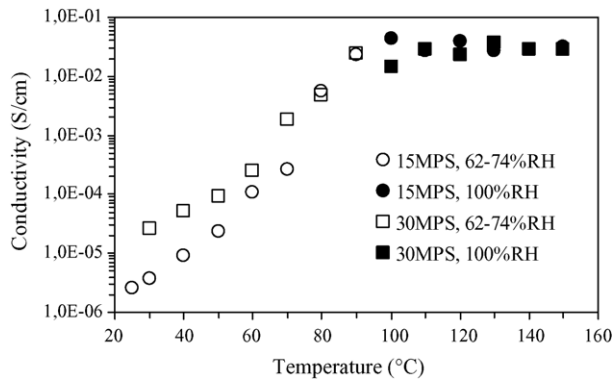


Fig. 5. Conductivity values as a function of temperature and relative humidity of the two hybrid membranes with 0.5 M % PWA.

higher conductivity is observed in the membrane with higher percentage of MPS at temperatures below 80 °C. The explanation is the higher number of hydroxyl groups in this membrane with a better capacity to adsorb and retain water by hydrogen bonds. 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 SiO₂ and PWA as a part of the structure, the materials can be high temperature tolerant proton-conducting membranes. The samples measured at 100% RH maintain a high value of conductivity ($3 \times 10^{-2} \text{ S cm}^{-1}$) at temperatures higher than 100 °C due to the water retention capability of SiO₂ and PWA. This behaviour is important in the objective of preparation of PEMFC membranes working at temperatures higher than 100 °C. The increase of conductivity with temperature up to 100 °C and the constancy of these values above this temperature suggest 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. This is the predominant factor up to 100 °C. The behaviour of conductivity above this temperature suggests compensation between the two trends, the thermally stimulated process of increase of conductivity with temperature and the higher dehydration of the membrane with higher temperature. Thus, it is very important the capacity to retain water at higher temperatures. The incorporation of SiO₂ improves the water retention at high temperature of the hybrid membrane increasing the high thermal stability of proton conductivity. A similar trend is observed with Nafion membranes. The modification of these membranes with sol-gel oxides based on SiO₂ has shown a significant improvement in fuel cell tests. The cell potentials and current densities at 130 °C are greater than those obtained with unmodified Nafion at 80 °C [6,7].

Membranes with 1.5 M % PWA (Fig. 6) presents a similar behaviour of variation of conductivity with temperature and relative humidity. The trends observed in Fig. 5 with membranes containing 0.5 M % PWA repeat in this case: increase

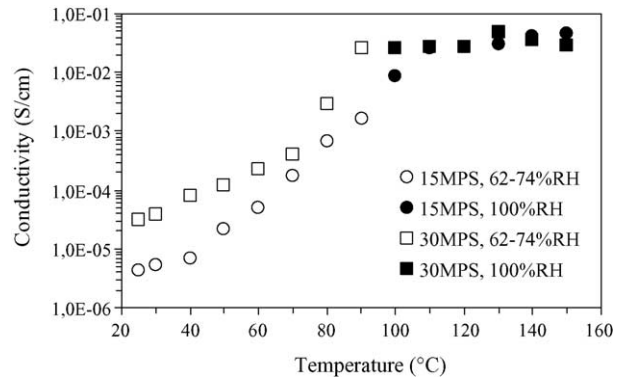


Fig. 6. Conductivity values as a function of temperature and relative humidity of the two hybrid membranes with 1.5 M % PWA.

of conductivity with temperature up to 100 °C and similar values above this temperature, and slightly higher conductivities below 80 °C in the membrane with higher percentage of MPS. The maximum conductivity values reached are also similar ($3 \times 10^{-2} \text{ S cm}^{-1}$) showing that an amount of 0.5 M % of PWA is enough to build well-connected paths for proton conduction.

4. Conclusions

Hybrid organic/inorganic membranes of methacrylate-silica covalent materials have been synthesised by polymerization of 2-hydroxyethyl methacrylate and 3-methacryloxypropyl trimethoxysilane, and hydrolysis-polycondensation of alkoxide radicals. Tungstophosphoric acid hydrate was incorporated to endow the membranes of proton conductivity. Structural analysis by FT-IR suggests that tungstophosphoric acid interacts with SiO₂ and hydroxyl groups from 2-hydroxyethyl methacrylate through an acid-base reaction. The water retention properties provided by SiO₂ and tungstophosphoric acid leads to high proton conductivity (maximum values around $3 \times 10^{-2} \text{ S cm}^{-1}$) at 100–150 °C. A 0.5 M % of PWA is enough to build well-connected paths for proton conduction.

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