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Epoxy-polystyrene-silica sol-gel membranes with high proton conductivity by combination of sulfonation and tungstophosphoric acid doping

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Abstract

New hybrid electrolytes based on 2-allylphenol (AP), (3-glycidoxypopyl) trimethoxysilane (GPTMS) and tetraethoxysilane (TEOS) have been synthesized by sol-gel method and organic polymerisation. Proton conductivity has been endowed on the base of three strategies: a high concentration of hydroxyl groups from the inorganic component, SO_3^- groups through sulfonation of phenyl rings, and incorporation of tungstophosphoric acid (PWA). The system AP-GPTMS-TEOS doped with PWA allows to obtain homogeneous, flexible, transparent and crack-free membranes after sulfonation of phenyl rings from AP. Membranes characterization includes degree of sulfonation, ion exchange capacity, water uptake and proton conductivity. TGA-DTA analysis shows that the hybrid membranes are thermally stable up to 190°C. Chemical stability of hybrid membrane against sulfonation and doping processes was demonstrated by FTIR and UV-Visible-NIR. The membranes present a high ion exchange capacity, similar to the Nafion[®], and water absorptions below 10%. Conductivities around 10^{-3} S/cm have been obtained at 40°C and 65 % relative humidity and $3 \cdot 10^{-3}$ S/m at 110°C and 100% RH. These results show that this new kind of hybrid membranes possess good

mechanical properties, high thermal and oxidative stability and high proton conductivity, making them an alternative to be used as electrolytes up to 150°C in PEM fuel cells as well as for lower temperatures and humidity (40°C, 65% RH).

Keywords: PEMFC; sol-gel; proton conductivity; PWA; sulfonation.

1. Introduction

Nafion[®] is the most studied material as electrolyte in proton exchange membrane fuel cells (PEMFC) due to its good characteristics and high stability in fuel cell environment [1].

However, these perfluorinated polymers can only be used up to 80°C because the loss of water at higher temperatures leads to a significant conductivity falling. Therefore, many efforts have been focused on the development of low-cost alternative proton conductive membranes [2,3]. In the last few years, proton conducting hybrid membranes prepared by sol-gel have been tested as promising candidates for PEMFC due to their attractive properties. Major motivations for this intense interest on alternative hybrid membranes are the high cost of Nafion[®] membranes, their limitations in cell operation temperature and humidity, the related weak tolerance of the Pt catalysts to CO, as well as the need to develop more efficient cooling systems [4]. The main requirements to be accomplished by alternative electrolytes used in PEMFC are: high proton conductivity, high thermal stability, good mechanical properties and ductility to support handling and pressures, easy way of preparation and long-term lifetime [5].

Hybrid membranes can be considered as bi-component materials, where at least one of the components, organic and/or inorganic is present and mixed at nanometer scale. The flexibility of the sol-gel synthesis approach offers the potential for molecular engineering of compositions and properties of a wide range of materials [6,7]. The presence of organic

components in the hybrid materials provides flexibility while their thermal stability is greatly enhanced by inorganic part.

Sulfonation reaction is a frequently used method for polymer modification in order to get better membrane properties such as higher hydrophilicity, higher water flux, improved permeability and high proton conductivity. The SO_3^- groups are attached to aromatic rings by direct sulfonation of the membranes [8,9]. This process is carried out in heterogeneous media using sulfonation agents. Sometimes, the use of strong sulfonating agents as chlorosulfonic acid provokes phase separation, crosslinking, side reactions and structural degradation, also producing water soluble membranes with a high sulfonation degree [10,11]. In this work, trimethylsilylchlorosulfonate was used as an alternative method for sulfonation [12]. This agent does not usually induce chain cleavage, even at high sulfonation degree, but it is less efficient than chlorosulfonic acid. In a previous work [13], we prepared hybrid membranes by sol-gel where the conductivity was provided by sulfonation of aromatic rings. These membranes exhibited maximum conductivities of $1.3 \cdot 10^{-3}$ S/cm at 140°C and 100% relative humidity. However, the decreasing of relative humidity (RH) led to a significant drop of conductivity (10^{-6} S/cm at 40°C and 65% RH). We demonstrated that it is possible to control the sulfonation degree to obtain an adequate combination of high ionic conductivity, good mechanical strength and a reasonably low affinity to methanol, avoiding the formation of water soluble materials; the proton conductivity being proportional to the concentration of mobile protons within the membrane.

In this context, a possible way to increase the proton conductivity without increasing the sulfonation level is the doping with appropriate acid solid heteropolyacids, able to increase the proton concentration via proton-transfer reactions. Heteropolyacids have already been used in PEMFCs or direct methanol fuel cells (DMFC) with polymer [14-17] and inorganic matrices [18-24]. Specifically, tungstophosphoric acid, $\text{H}_3(\text{P}(\text{W}_3\text{O}_{10})_4)$ (PWA) forms channels

that contain up to 29 water molecules in different hydrate phases. This variety leads to different stable proton species (up to 180°C) and hydrogen bonds of different strength; the result is high proton conductivity at room temperature. However, heteropolyacid electrolytes usually dissolve in the water produced in the fuel cell [25,26]. To overcome the dissolution of heteropolyacids and the consequent shorter lifetime of the fuel cell, PWA should be incorporated in host materials such as hybrid networks in which PWA clusters can be stabilised through strong Coulombic interaction with the inorganic part of the hybrid framework [20].

This paper describes the synthesis and properties of inorganic-organic hybrid membranes in the system tetraethyl orthosilicate (TEOS) - 3-glycidoxipropyl trimetoxysilane (GPTMS) - 2-allylphenol (AP) doped with PWA [6,13]. The organo-alkoxysilanes, GPTMS and TEOS, generate an inorganic matrix through hydrolysis and polycondensation of Si-OCH₃ and Si-OC₂H₅ groups yielding three dimensional Si-O-Si linkages, which increase the thermal and chemical stability of the membranes. Additionally, the hybrid (GPTMS) and organic (AP) precursors undergo organic polymerisation improving the flexibility and ductility of the membranes [13, 27-30]. On the other hand, AP provides phenyl groups that increase the thermal stability permitting the incorporation of SO₃⁻ groups through sulfonation, as well as promoting a higher hydrophilic behaviour due the presence of hydroxyl groups. Three different methods are able to supply high proton conductivity in this hybrid material: free hydroxyl groups, SO₃⁻ groups from sulfonation of aromatic rings and heteropolyacid doping. An illustration of the hybrid structure can be observed in Fig. 1, showing a channel containing PWA molecules and the movement of protons jumping from one hopping site to another.

The main objective was to overcome the drop of conductivity observed when the relative humidity becomes lower than 100% in order to reduce the problems associated with the water

management in the fuel cell. On the other hand, a low dependence of the conductivity with the temperature between room temperature and 110°C is the other important aim of this work.

The nanostructured network and the multiple hopping sites provided should make it possible to retain enough water molecules inside the structure when the relative humidity is too low for a typical water-base proton transport mechanism. SEM, TGA-DTA, FTIR, UV-Visible-NIR, water adsorption, ion exchange capacity and EIS techniques have been used for characterising the obtained membranes.

2. Experimental

Materials: Tetraethyl orthosilicate (TEOS) and 3-glycidoxipropyl trimetoxysilane (GPTMS) from ABCR, and 2-allylphenol (AP) and tungstophosphoric acid hydrate (PWA) from Fluka were used as precursors.

Synthesis: The sol (molar composition: 20 TEOS – 39.3 GPTMS – 40 AP – 0.7 PWA) was prepared by mixing two solutions. Solution A was prepared by mixing absolute ethanol (molar ratio of ethanol/AP = 2), calculated amounts of PWA and H₂O (molar ratio of water / (TEOS+GPTMS) = 3.5), stirring at room temperature for 30 minutes. Solution B was prepared by stirring at room temperature for 30 minutes a mixture of AP and 2,2'-azobis(isobutyronitrile) (AIBN, from Fluka) (0.85 wt% respecting to AP) as initiator of the free-radical copolymerisation. Afterwards, TEOS and GPTMS were incorporated in solution B stirring at room temperature for 15 minutes. Both solutions were mixed and stirred at room temperature for another 60 minutes. In this synthesis procedure, no further acid was added since PWA acts as acidic catalyst besides donating proton carriers for conduction.

Sols were cast in polytetrafluoroethylene moulds and left at 60°C for obtaining homogeneous gels through copolymerisation of GPTMS and AP, and simultaneous sol-gel reactions of GPTMS and TEOS. Hybrid membranes were additionally treated at 110°C (heating rate 0.1°C/min) in air for 24 hours to complete the drying and curing processes. The membranes

were sulfonated by immersion between 2 and 24 hours in 0.3 M solution of trimethylsilylchlorosulfonate ((CH₃)₃SiSO₃Cl) (from Aldrich) in 1,2-dichloroethane.

Analytical methods: The fracture surface of the membranes was examined with a HITACHI S-4700 field emission scanning electron microscope (FE-SEM). Elemental analysis by EDX (NORAN system six) was used to study the distribution of elements across the membrane thickness. Thermal stability of the membranes dried at 110°C was studied by Thermogravimetric Analysis (DTA-TGA) in air up to 900°C with a heating rate of 10°C/min using a Netzsch STA 409. FTIR spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer in the 650- 4000 cm⁻¹ range using the Attenuated Total Reflectance (ATR) accessory with a resolution of 2 cm⁻¹. Moreover, UV-Visible-NIR spectra were recorded between 2500- 2000 nm with a spectrophotometer Perkin Elmer (Lambda 950), with a resolution of 2 nm. Water absorption tests were performed using weight changes before and after soaking the membranes in deionized water at room temperature for 24 hours. The water absorption (WA) was calculated by $WA (\%) = [(W_{wet} (g) - W_{dry} (g)) / W_{dry} (g)] 100$, where W_{wet} and W_{dry} are the weight of wet and dried samples, respectively. The Ionic Exchange Capacity (IEC) of the hybrid membrane was determined by acid-base titrations. The EIC was calculated according to $IEC = nH^+ / W_{dry}$, where IEC (mmol·g⁻¹) is the number of milimoles of H⁺ (nH⁺) per membrane weight. Membranes were converted to H⁺ ionic form by immersion in HCl 1 N for 24 hours. Afterwards, they were soaked in 50 ml of NaCl 1 M for another 24 hours to produce the exchange of protons and sodium ions. Finally, 50 ml of the solution was titrated with NaOH 0.005 M until equivalent point. Membranes were regenerated with 0.1 N HCl, washed with water and dried up to a constant weight using a vacuum oven at 80°C. Elemental analysis (C, H, N, S) was done using a LECO CHNS-932 in order to determine the sulfonation level of membranes. The conductivity of hybrid membranes was measured by Electrochemical Impedance Spectroscopy (EIS) using a Gamry FAS2 Femtostat with a two-

electrodes device, silver electrodes and a frequency range of 1 to 10^5 Hz. 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 hours inside a sealed chamber containing a saturated solution of NaNO_3 for the 62-70% range (temperatures lower than 50°C), 70-81% range (temperature between 50 and 70°C), 81-99% range (temperatures between 70 and 90°C) and water vapour for the 100% (temperatures higher than 90°C). Then, conductivity measurements were performed at different temperatures and relative humidity. Both parameters have been measured using a Rotronic HYGROCLIP HK 25 [31]. Membranes doped and sulfonated for 6h were immersed in water at room temperature for 45 days; afterward, the conductivity was measured as a function of temperature and relative humidity to investigate the possible release of the doping agent.

3. Results and discussion

3.1. Structural characterization

The hybrid membranes are homogeneous, transparent and crack-free, with orange colour after the polymerisation process at 60°C that turn to brown after the thermal treatment at 110°C . The sulfonation process of membranes with $(\text{CH}_3)_3\text{SiSO}_3\text{Cl}$ solutions does not produce appreciable changes. Fig. 2 shows a photograph of a hybrid membrane treated at 110°C and sulfonated for 6 hours. The high homogeneity observed suggests no phase separation indicating that the organic and inorganic components were blended at molecular level. SEM microphotographs (Fig. 3) display a very smooth and homogeneous surface for membranes without sulfonation, and sulfonated for 24 hours. The Fig. 3 a) is an image of the fracture surface of a membrane without sulfonation showing a homogeneous material formed by nanosized agglomerates, between 25-50 nm without phase separation, and a low size porosity (5-10 nm), very important to retain water molecules and maintain high values of proton

conductivity at low humidity. The membrane that combines PWA and sulfonation for 24 hours (Fig. 3b) presents a slight superficial degradation due to sulfonation reaction. EDX analyses (mapping of S and W) present a homogeneous distribution of the elements across the membrane confirming that PWA and SO_3^- groups are well dispersed in the structure (not shown).

2.2. Thermal characterization

Thermal analysis is used to investigate the dehydration of the membranes and their thermal stability. TGA and DTA curves of membranes sulfonated for 2, 6 and 24 hours are presented in Fig. 4. The membranes show analogous behaviours showing four main ranges of weight losses. The first region, between room temperature and 190°C , presents a weight loss of 8% and an endothermic peak at 150°C associated with the desorption of physically absorbed water, residual solvents and a part of the structural water from PWA (that maintains 6 water molecules) [32]. The second region, between 190°C and 300°C , shows a weight loss of 8% and a second endothermic peak at 250°C . Both are assigned to the final loss of water from PWA, which becomes anhydrous, along with the loss of water and residual solvents generated in the sol-gel reactions and SO_3^- groups. Park et al. [33] investigated the thermal stability of sulfonated membranes using thermogravimetric analysis-mass spectrometry (TGA-MS). They found that the evolution of SO_2 and SO gases due to desulfonation process started at temperatures higher than 200°C . Similar findings were also reported in previous studies [17,23,34] performed on non-perfluorinated and perfluorosulfonate ionomers. The third region, between 300 and 450°C , presents an important weight loss (15%) and an exothermic peak at 330°C assigned to the partial combustion of the organic component, mainly epoxy and polyethylene oxide (PEO) chains. In the fourth region, between 450 and 650°C , a double exothermic peak at 496 and 540°C , and a weight loss of 24% can be observed. The first peak is assigned to the structure collapse of PWA due to phosphorus loss and the final

decomposition of the polymeric chains and tri-substituted aromatic rings, while the second peak is due to combustion of di-substituted aromatic rings [13]. Comparing the curves, it is observed that the intensity of the peak at 540°C decreases with the sulfonation time, meaning that sulfonation process has been developed in a higher extension. Based on these results, the thermal stability of the membranes can be fixed at around 250°C, without significant degradation of the hybrid structure developed. However, the weight loss observed at lower temperature assigned to critical groups for proton conduction, as water molecules from PWA and SO_3^- groups reduces the maximum operation temperature of these membranes for PEMFC application at values of 150°C.

2.3. Chemical characterization

FTIR spectra were carried out in order to elucidate the interactions between polymer network, inorganic oxides and heteropolyacid clusters. Fig. 5 shows the FTIR spectra of pure PWA (precursor as purchased) and membranes without (only doped, called “PWA”) and with sulfonation for different times in the 1200-700 cm^{-1} spectra range. Assignments of the main bands (Table 1) are based on literature values [8,11,13,15-17]. There are clear evidences showing the retention of the Keggin ion structure in the membrane. The group of frequencies corresponding to the W_3O_{13} triads in the membrane are very similar to those observed in the pure PWA, but appear partially overlapped with the Si-O frame vibrations and some bands corresponding to $-\text{SO}_3\text{H}$ groups. The broad corner-sharing W-O_c-W band at 760 cm^{-1} in pure PWA is shifted to around 810 cm^{-1} when PWA is incorporated in the membrane structure. On the other hand, a small shift of the edge-sharing W-O_b-W band is observed from 885 cm^{-1} in pure PWA to 895 cm^{-1} in the hybrid membranes. No change was observed in the position of the band related to P=O bond at 1075 cm^{-1} and that at 970 cm^{-1} related to W-O vibration mode. Frequency shifts of W-O_c-W and W-O_b-W bands have been correlated with the

strength of anion–anion interactions, which take place due to the electrostatic repulsion between the PWA anions in the structure [35]. The increase of these anion–anion interactions with increasing distance between oxygens of neighbouring PWA anions has been observed. These shifts might be due to the interaction through hydrogen bonds between the corner oxygen of the PWA molecules and the inorganic network and SO₃H groups [36]. No band is observed at 1260 cm⁻¹, the frequency assigned to the epoxy rings, suggesting that have disappeared after the hydrolysis reaction to form the pseudo-PEO network. It has been also found for all hybrid membranes that band assigned to C=C vibration appearing at 1629 cm⁻¹ is almost negligible (not shown), indicating that the organic radical polymerization of AP was practically complete. To confirm the polymerisation of the epoxy rings, UV-Visible-NIR spectra were also performed in hybrid membranes. Fig. 6 shows the UV-Visible-NIR absorption spectra of GPTMS precursor and membranes without and with sulfonation at different times in the 2150-2250 nm range. The absorption spectrum of GPTMS is characterised by an isolated and narrow peak at around 2208 nm assigned to epoxy ring [37]. This band does not appear in the hybrid membranes confirming that the cationic polymerisation is completed. Since the hybrid network is constructed from two different polymerising mechanisms (radical polymerisation of AP C=C double bonds and opening of the epoxy group of GPTMS), it is reasonable to expect a rather open structure, with lower density related to networks coming from a unique polymerisation mechanism. In this type of structure, more suitable for retaining water molecules, PWA will likely find an easier way to accommodate itself in the network interstices and interacts with the inorganic species, through hydrogen bonds with OH groups.

2.4. Proton conduction properties

2.4.1. Ion exchange capacity and water absorption

The ion-exchange capacity (IEC) of the membranes was determined by titration. Proton conductivity and water content depend on the concentration of ionic domains in the hybrid membrane. Water absorption (wt %) of the membranes is also a very important factor because the proton transport is associated with water molecules in this type of materials. The results of IEC, water absorption and S content are presented in Table 2. IEC increases with the sulfonation time, suggesting a higher extension of the sulfonation reaction. It becomes as high as 0.6 meq/ g when the membrane is only doped with PWA. The combination of PWA doping and sulfonation produces a maximum value of 1.1 meq/ g for a sulfonation time of 24 h. This increasing trend is analogous to that observed in the elemental analysis results (Table 2), confirming the increasing of sulfonation with the immersion time. Water absorption follows a similar behaviour, increasing with the sulfonation time. However, the water absorption of these membranes is lower compared with other hybrid sulfonated membranes [13]. This can be attributed to the strong interaction between SO_3^- groups and PWA molecules, which decreases the number of water absorption sites [38-39]. Although the maximum values of IEC and water absorption were obtained for membranes sulfonated for 24 hours, this degree of sulfonation leads to a lower chemical stability and the beginning of the membrane degradation. Indeed, a crucial factor is the control of the sulfonation reaction for obtaining membranes with high proton conductivity, but also with a high chemical and mechanical stability. No swelling was detected during the water absorption test in any hybrid membrane, probably due to the chemical structure with strong Si-O-Si bonds.

2.4.2. Proton conductivity

Fig. 7 presents the Nyquist plots of a hybrid membrane sulfonated for 6 hours at different temperature and relative humidity between 62 and 100%. The diagrams show part of semicircles at high frequencies associated with the capacitance of the membrane in parallel

with its pore resistance, and correspond to the bulk electrical properties. A second time constant appears in the low frequencies region due to the electrodes-membrane interface and diffusion processes. The increase of temperature and relative humidity originates a reduction of the amplitude of the high frequencies semicircle associated with a higher conductivity. The conductivity σ of the samples, measured across the membrane, 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 high frequency semicircle with the $\text{Re}(z)$ axis calculated using Echem Analyst software of Gamry for fitting the curves. Conductivity measurements were performed three times and average value was taken in order to obtain a high stability, reproducibility and accuracy value of the resistance in the direction of thickness of the membrane. The shape of the Nyquist spectra suggests the presence of only one proton conducting mechanism, where the water molecules are the vehicle that allows the movement of protons through the membrane. In membranes without sulfonation, the water molecules of the Keggin units from PWA and hydroxyl groups of the hybrid network are the responsible for the proton transfer across the membrane. The additional sulfonation process incorporates new hopping points for protons, further increasing the conductivity. The presence of PWA increases the acidity of the sulfonic groups and enhances the water retention and proton conduction.

Fig. 8 illustrates the conductivity values of hybrid membranes without sulfonation and sulfonated at different times as a function of temperature and relative humidity. Proton conductivity in these membranes can be explained through a thermal and humidity stimulated process. A higher relative humidity likely originates an increase of the water absorbed on active positions such as hydroxyl groups, sulfonate groups and PWA Keggin units attached to the hybrid network, enhancing the transport of protons through the material. On the other hand, the Arrhenius equation predicts an increase of proton conductivity with temperature,

without taking into account other parameters as dehydration of the membrane when the temperature rises. For most sulfonated polymer membranes, the conductivity decreases when temperature is higher than 100°C due to the water loss. The incorporation of PWA is a method to improve the capacity of membranes to retain water even at low relative humidity because some of the structural water molecules are stable up to 180°C. The additional ionic domains (SO_3^-) incorporated with the sulfonation process produces a proton conductivity increasing. For 2 hours of sulfonation, the proton conductivity slightly increases compared with the sample without sulfonation. However, the increase of sulfonation time up to 6 and 24 hours produces a significant improvement of proton conductivity, mainly at low temperature and low relative humidity. The best results were obtained for membranes sulfonated for 6 hours, with conductivity values higher than 10^{-3} S/cm at temperatures lower than 50°C and relative humidity lower than 70%. The membrane with 24 h of sulfonation presents a lower conductivity compared with the 6h sulfonated membrane, probably because of the surface degradation observed by SEM.

Fig. 9 compares the conductivity of a hybrid membrane only doped with PWA, one only sulfonated for 2h [13] and one combining PWA doping and 6 h of sulfonation as a function of temperature and relative humidity. Conductivity increases with temperature and relative humidity as usual, but a significant increase of proton conductivity is observed when the number of ionic domains (PWA and SO_3^- groups) increases. The proton conductivity can be directly related to the concentration and acid strength of surface groups in presence of inorganic additives such as heteropolyacids [32]. The membrane containing a combination of both processes presents a proton conductivity three orders of magnitude higher than that of only sulfonated membrane at low temperature and relative humidity. At high temperature and 100 % RH, proton conductivities become similar for all the membranes because in these conditions water molecules fill all the pores facilitating the proton transfer. Sulfonated

membrane needs a higher temperature and 100 % RH to effectively reach enough proton conductivity, meaning that a high amount of water molecules are necessary to hydrate the sulfonated groups and connect them in the proton transfer channels. The interaction between PWA and sulfonic groups in hybrid membranes is a Brönsted type, where PWA plays the acid role and SO_3^- groups act as a base [40]. The free protons in the PWA molecule interact with the sulfonic acid groups forming protonated sulfonic acid groups, such as $-\text{SO}_3\text{H}_2^+$. The transport of the protons is mainly explained by the Grothuss mechanism, likely taking place from the protonated SO_3H to a deprotonated group, assisted by H_2O molecules (as H_3O^+). The maximum value of proton conductivity obtained, 10^{-2} S/cm at 110°C and 100% RH, confirms the compatibility and synergy of the process involved in proton transport. These results are promising and open new possibilities of applications for these membranes in electronic devices working at low temperature and RH.

2.4.3. Long-term stability

A main concern about the incorporation of PWA to membranes in order to increase the proton conductivity is related to the possible leaching of this heteropolyacid in the water generated in the cathode of the fuel cell, producing a rapid drop of proton conductivity. Hybrid membranes sulfonated for 6 h were tested after immersion in water at room temperature up to 45 days. The proton conductivity was measured as a function of temperature and relative humidity after different immersion times (Fig. 10). As observed, the conductivity of the hybrid membrane was not practically affected by the long storage in water. Proton conductivities of the hybrid membrane maintained its high values (between $1.5 \cdot 10^{-3}$ and $2.0 \cdot 10^{-3}$ S/cm), confirming that these membranes present high stability in full hydrated condition during long periods. This behaviour reveals that PWA can be stabilised in the hybrid network for a long term due to the interactions between Keggin ions and hybrid network, and the homogeneous

distribution of the heteropolyacids in the membrane, two facts that have been confirmed by EDX and FTIR analysis.

3. Conclusions

Epoxy-polystyrene-silica sol-gel membranes doped with tungstophosphoric acid and further sulfonated have been successfully prepared by sol-gel technique and organic copolymerisation. The heteropolyacid has been immobilised within the membranes through electrostatic interaction with SO_3^- and hybrid network, overcoming the leakage problem from membranes. The homogeneous hybrid membranes show thermal stability up to 150°C , to avoid the loss of sulfonate groups and structural water from the heteropolyacid, and high water uptake and ion exchange capacity. FTIR spectra indicate the preservation of the Keggin ion geometry in the hybrid membranes and its interaction with the hybrid membrane. The membranes doped with tungstophosphoric acid and sulfonated for 6 h exhibit the highest proton conductivity in all the temperature range. In particular, the high conductivity values reached at low temperature and low relative humidity, 10^{-3} S /cm at 40°C and 65 % RH, can be considered a significant improvement in these conditions. It is worth to mention that conductivity of the hybrid membranes was not affected by storage in water up to 45 days, demonstrating the interaction of the heteropolyacid with the network and preventing its leakage. Therefore, these hybrid membranes are promising proton-conducting materials and have a great potential for application in PEMFCs working up to 110°C , but in particular at low temperature and relative humidity.

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Fig. 1. Illustration of the hybrid structure simulating the protons transfers, where: represented water molecules, protons, and hydrated Keggin ions.

Fig. 2. Photograph of a hybrid membrane treated at 110°C and sulfonated for 6 h.

Fig. 3. FE-SEM photographs of a fracture surface: a) hybrid membrane without additional sulfonation and b) hybrid membrane sulfonated for 24 h.

Fig. 4. TGA and DTA curves of hybrid membranes treated at 110°C and sulfonated for 2, 6 and 24 h.

Fig. 5. FTIR spectra of commercial phosphowolframic acid “pure PWA” and hybrid membranes without and with sulfonation for 2 and 24 h.

Fig. 6. NIR spectra of GPTMS precursor and hybrid membranes without and with sulfonation for 2 and 24 h.

Fig. 7. Nyquist plots of the hybrid membrane sulfonated for 6 h at different temperatures and relative humidities.

Fig. 8. Conductivity values of the hybrid membranes without sulfonation and sulfonated for 2, 6 and 24 h, as a function of temperature in different humidity ranges.

Fig. 9. Conductivity values as a function of temperature in different humidity range of the hybrid membranes sulfonated for 2h, only doped with PWA and, doped and sulfonated for 6 h.

Fig. 10. Proton conductivity as a function of temperature and relative humidity for a membrane doped and sulfonated for 6h and immersed in water at room temperature up to 45 days.

Precursor	Vibration frequency (cm ⁻¹)	Bond assignments
PWA	1638	δ OH
	1075	δ P=O
	971	ν W-O _a
	895	ν W-O _b -W
	740	ν W-O _c -W
SO ₃ ⁻	920	δ R-SO ₂ ⁻
	707; 880	δ S-O
GPTMS/ TEOS	2995-3050	ν CH
	1370-1480	ν CH ₃
	1420	δ CH ₂
	1240-1260; 912	ν epoxi
	1197	ν Si-O-Et
	816	ν Si-O-CH ₃
	784	δ Si-O-Et
AP	1423, 1191	δ C-H aromatic
	999	δ ring
	793, 730	δ C-H
Hybrid network	1483, 1393, 1365	ν_s C-O-C, ν C-C
	1175	ν_{as} Si-O-C
	1100-1040	ν Si-O-Si ν C-O-C
	980	ν Si-OH
	949	δ Si-O
	750	δ Si-O-Si

Table 1. Assignments of the main absorption bands.

Composition	IEC (meq/g)	Water adsorptions (%)	Elemental analysis S (%)
PWA	0.60±0.05	5.4±0.2	-
PWA+S-2h	0.73±0.05	8.0±0.2	0.70±0.02
PWA+S-6h	0.90±0.05	8.5±0.2	2.12±0.02
PWA+S-24h	1.11±0.05	9.6±0.2	2.90±0.02

Table 2. Ion exchange capacity (IEC), water absorption and elemental analysis of S of hybrid membranes.