

Short communication

Synthesis and characterization of proton-conducting sol–gel membranes produced from 1,4-bis(triethoxysilyl)benzene and (3-glycidoxypropyl)trimethoxysilane

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Abstract

Hybrid membranes using 1,4-bis(triethoxysilyl)benzene and (3-glycidoxypropyl)trimethoxysilane have been synthesised by polymerization of epoxy groups and inorganic condensation of silanol groups. Sulfonation processes of aromatic rings to produce attached SO₃H groups are applied to provide proton conductivity. Thermal analysis shows a high water adsorption capacity combining SO₃⁻ and silanol groups. The measurement of conductivity shows a general increase with temperature, and stabilization at temperatures above 100 °C. This behaviour suggests the presence of two competing trends, one enhancing (thermal activation) and the other reducing (dehydration) conductivity. The water retention properties provided by SO₃⁻ and silanol groups lead to relatively high proton conductivity (maximum values around 8.5×10^{-4} S cm⁻¹) at 100–150 °C.

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1. Introduction

There is a great interest in proton-exchange membrane fuel cells (PEMFC) for different applications, especially for transportation. Compared to internal combustion engines, 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). Also, these membranes remain expensive and have several limiting factors, such as low conductivity at low relative humidity, high methanol permeability and a low glass transition temperature (T_g), which restrict their application to below 100 °C [1,2]. 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]. Moreover, the increase of PEMFC operation temperature would allow increased fuel cell reaction kinetics and lower consumption of platinum catalyst, and direct use of low-temperature fuels, such as methanol [3–5].

Nano-structured materials consisting of organic and inorganic components are an interesting alternative to polymeric membranes in order to reach higher PEMFC operation temperature. 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, although a greater fragility is usually associated with high inorganic content [6,7]. A compromise between all these properties has to be achieved to produce adequate proton-conducting membranes with application in PEMFC.

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Hybrid compounds made by the formation of siloxane (Si–O–Si) bonds are an important body of materials in this field, ranging from inorganic silicates to organically modified polysiloxanes. All of these siloxane-based materials are prepared by hydrolysis and condensation reactions of sol–gel precursors [8]. When the mechanical stability is an important parameter, as in case of the preparation of membranes with thickness below 200 μm , one or more additional polymerizable groups must be attached to the silicon to permit polymeric cross-linking, and also combine with monomers. The homogeneity of the inorganic and organic phases allows for molecular engineering of the bulk properties of the hybrid organic/inorganic materials without nano-scale phase separation. 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 (DMFC) [9].

The aim of this work has been a practical synthesis of 1,4-bis(triethoxysilyl)benzene, and the preparation and characterization of proton-conducting organic/inorganic membranes using this compound and (3-glycidoxypropyl)trimethoxysilane. Both of them can polymerize through hydrolysis and condensation reactions to produce a Si–O–Si network. The latter has also an epoxy group in its structure that permits an organic polymerization in order to produce a more flexible material. 1,4-Bis(triethoxysilyl)benzene contains an aromatic ring attached to silicon atom suitable for a sulfonation process to produce SO_3^- groups responsible for high proton conductivity. Two different sulfonating agents have been used in this process: chlorosulfonic acid and trimethylsilyl chlorosulfonate. The former is a strong sulfonating agent that can produce side reactions including cross-linking and cleavage of the polymer chains. Trimethylsilyl chlorosulfonate does not usually induce chain cleavage, even at high sulfonation degree [10–13]. The optimal composition and synthesis conditions to promote organic polymerization and sol–gel condensation, avoiding phase separation, are important issues of this work. Thermogravimetric analysis (TGA), differential thermal analysis (DTA), Fourier transform infrared spectroscopy (FT-IR) and electrochemical impedance spectroscopy (EIS) have been used for characterising the membranes obtained.

2. Experimental

2.1. Synthesis of 1,4-bis(triethoxysilyl)benzene (BTESB)

All the reagents were used without further purification [14,15]. 18.4 g of 1,4-dibromobenzene from Aldrich in 50 ml of THF from Aldrich was added dropwise under ultrasound waves to a mixture of 160 ml of TEOS from ABCR, 60 ml of THF, 6 g of magnesium and a single crystal of iodine previously mixed at 75 °C. After few minutes, the reaction

mixture started to reflux and the addition rate was adapted for a mild reflux. After addition, heating was maintained for 2 h. The cooled reaction mixture was concentrated “in vacuo”, and residue was extracted with hexane (4 \times 40 ml). The solvent was stirred for 2 h at room temperature, filtered and evaporated under low pressure. The crude was distilled to yield 31.7 g (79%, based on dibromobenzene, 180–190 °C/2 mmHg). The purity of the product was confirmed by GC–MS and NMR.

2.2. Preparation of proton-conducting organic/inorganic membranes

The second precursor used on the preparation of the hybrid membranes is (3-glycidoxypropyl)trimethoxysilane (GPTMS) from ABCR. Two compositions were prepared, 100BTESB and 50BTESB–50GPTMS. Sols were prepared by mixing both precursors with absolute ethanol (molar ratio of ethanol/BTESB = 20) and HCl 1N with stirring for 15 and 90 min at room temperature for 100BTESB and 50BTESB–50GPTMS compositions, respectively. Two molar ratios of water/BTESB = 4 and 8 were also analyzed. Solutions with the same compositions and procedure but substituting half of the ethanol by formamide from Merck were also prepared and characterized. All the reagents were used without further purification.

The solutions were cast in glass and polytetrafluoroethylene moulds, and placed at room temperature up to the gel formation. The so-obtained hybrid membranes with thickness below 200 μm were further treated at 150 °C using a heating rate of 0.1 °C min^{-1} . Additionally, the membranes were sulfonated alternatively by immersion for 4 h in 0.3 M solutions of HSO_3Cl and $(\text{CH}_3)_3\text{SiSO}_3\text{Cl}$ in 1,2-dichloroethane. Then, membranes were washed in distilled water and dried at 50 °C for several hours.

2.3. Characterization of membranes

The thermal behaviour (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 (Perkin-Elmer model 1720X with a resolution of 2 cm^{-1} and a frequency range of 4000–400 cm^{-1}) was used to analyze crushed samples using KBr pellets. The conductivity of hybrid membranes treated at 150 °C was obtained by electrochemical impedance spectroscopy 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 NaNO_3 for the 64–75 RH% range, and water vapour for the 100 RH% [16]. The frequency was varied from 10 Hz to 10 MHz, and the EIS curves were resolved using equivalent circuit software [17].

3. Results and discussion

The 1,4-bis(triethoxysilyl)benzene has been prepared following an improved procedure by treatment of 1,4-dibromobenzene with magnesium under ultrasound waves for obtaining quantitatively a bis-Grignard complex that was reacted with TEOS, to give the bis-silyl derivative in excellent yield.

The gel time for compositions with water/BTESB = 4 was of 3 days, time that decreases to 2 days when the water/BTESB ratio was 8. This behaviour is based on the increase of hydrolysis reaction rate with the water concentration. All the hybrid membranes treated at 150 °C before the sulfonation processes are homogeneous, transparent and yellow coloured. The high homogeneity indicates no phase separation suggesting that the organic and inorganic components were blended at molecular level. Only the 100BTESB membranes present some cracks due to its higher inorganic component content compared with 50BTESB–50GPTMS membranes. The incorporation of formamide leads to bigger samples without cracks, although some cracks are always presented in the 100BTESB membranes. The sulfonation process of membranes with HSO₃Cl solution produces a partial loss of transparency and a change of membrane colour from yellow to brown on 50BTESB–50GPTMS membranes. On the other hand, this change in transparency and colour was less intense with the sulfonation process with (CH₃)₃SiSO₃Cl solution.

TGA–DTA curves of 100BTESB membranes with and without sulfonation process with HSO₃Cl and (CH₃)₃SiSO₃Cl in 1,2-dichloroethane are shown in Fig. 1. Only the DTA curve of membrane sulfonated with HSO₃Cl has been incorporated in order to simplify the figure. The thermogravimetric curve of the sample without sulfonation shows a weight loss of 10% between room temperature and 130 °C assigned to desorption of physically adsorbed water because of the presence of hydroxyl groups from Si–OH groups that can attract water molecules. The increase of temperature up to 500 °C originates an additional weight loss of 10% in this TGA curve associated with water and ethanol generated during the sol–gel reactions. Above 500 °C begins a continuous weight loss attributed to the combustion of aromatic rings.

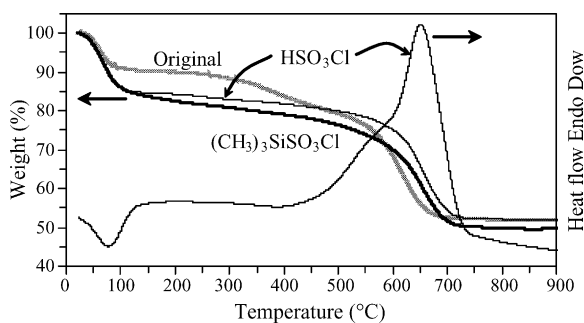


Fig. 1. TGA–DTA curves of 100BTESB membranes with and without sulfonation process with HSO₃Cl and (CH₃)₃SiSO₃Cl solutions.

The assignment of these weight loss variations is supported by the results of DTA curve (not shown in Fig. 1) with an endothermic peak at 90 °C, and two exothermic peaks at 550 and 670 °C. The incorporation of the sulfonation process produces some changes in the TGA–DTA curve (Fig. 1). The TGA curves of the membrane sulfonated with HSO₃Cl and (CH₃)₃SiSO₃Cl solutions show a higher weight loss at low temperature (16%), attributed to physically adsorbed water, compared with the membrane without sulfonation. This difference points out the first difference with the membrane without sulfonation process indicating that this process produces sulfonic groups attached to the aromatic rings that react with water. An endothermic peak at 90 °C confirms the evaporation of water bounded to the sulfonic and hydroxyl groups. The second step, between 150 and 270 °C, shows a small but continuous weight loss that is believed to be due to the decomposition of sulfonic acid groups [18–21], reducing the thermal stability up to 170 °C approximately. The last step, above 270 °C, shows a continuous weight loss attributed to the combustion of the polymeric component. Correspondingly, two exothermic peaks appear with maximum at 560 and 660 °C (Fig. 1).

Fig. 2 shows the TGA–DTA curves of 50BTESB–50GPTMS membranes with and without sulfonation process with HSO₃Cl and (CH₃)₃SiSO₃Cl in 1,2-dichloroethane. Only the DTA curve of membrane sulfonated with HSO₃Cl has been incorporated in order to simplify the figure. The thermal behaviour of these samples at temperatures below 150 °C is similar than that observed on 100BTESB membranes, i.e. a higher weight loss associated with water desorption on membranes sulfonated with HSO₃Cl or (CH₃)₃SiSO₃Cl solutions. The weight loss is smaller in this case (5%) because of the lower number of sulfonic groups attached to the aromatic rings. A broad and small endothermic peak at low temperature agrees with this behaviour. The incorporation of additional organic component (epoxy groups) compared with 100BTESB leads to changes in TGA–DTA curves. The weight loss at temperatures between 150 and 500 °C is significant (58%) in this case, and it is assigned to combustion of epoxy groups. DTA curves show two intense exothermic peaks at 280 and 410 °C that agree with the elimination of these groups (Fig. 2). The last weight loss at temperatures higher than 500 °C (19%) is assigned to the final decomposition of the polymeric network,

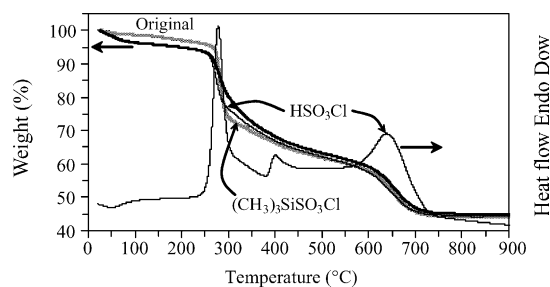


Fig. 2. TGA–DTA curves of 50BTESB–50GPTMS membranes with and without sulfonation process with HSO₃Cl and (CH₃)₃SiSO₃Cl solutions.

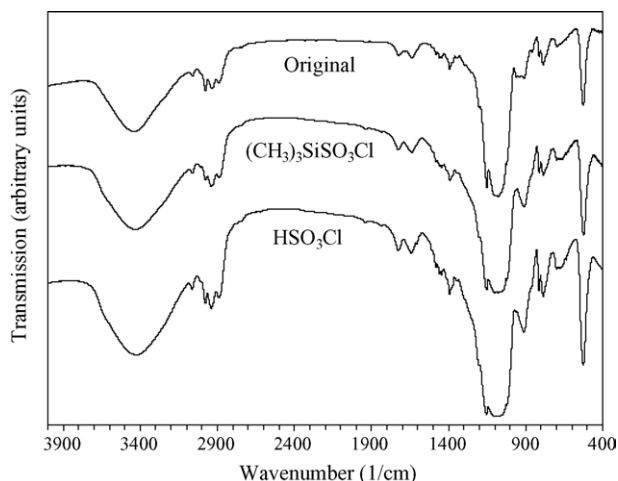


Fig. 3. FT-IR spectra of 50BTESB–50GPTMS membranes with and without sulfonation process with HSO₃Cl and (CH₃)₃SiSO₃Cl solutions.

mainly aromatic rings. A sharp exothermic peak centred at 650 °C corresponds to this weight loss.

Fig. 3 shows the FT-IR transmission spectra in the 4000–400 cm⁻¹ range of 50BTESB–50GPTMS membranes with and without sulfonation process with HSO₃Cl and (CH₃)₃SiSO₃Cl solutions. The spectra of the three samples are similar showing the high stability of the polymeric network to sulfonation processes. All the bands present in the spectra are in good agreement with those coming from precursors and are assigned using literature data [11–13]. The sulfonation process with both sulfonating agents' leads to a new peak (900 cm⁻¹) associated with the SO₃⁻ groups [18]. FT-IR transmission spectra of 100BTESB membranes with and without sulfonation process with HSO₃Cl and (CH₃)₃SiSO₃Cl solutions do not present any relevant variation.

The complex impedance spectra (Nyquist plot) present a semicircle through the origin at high frequencies with samples measured at temperatures up to 80 °C, and additional inclined lines at low frequencies when samples are measured at temperatures higher than 80 °C. As an example, Fig. 4 shows the Nyquist plots at different temperatures in the 64–100 RH% range of a 100BTESB membrane sulfonated with the (CH₃)₃SiSO₃Cl solution. 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 $\sigma = t/RS$. In this equation, t and S are the thickness and electrode area of the sample, respectively. R was obtained from the intersection of the semicircle with the Re(z) axis calculated using the equivalent circuit software [17]. The increase of temperature leads to smaller semicircles (resistance reduction) because proton conductivity is in general a thermally stimulated process.

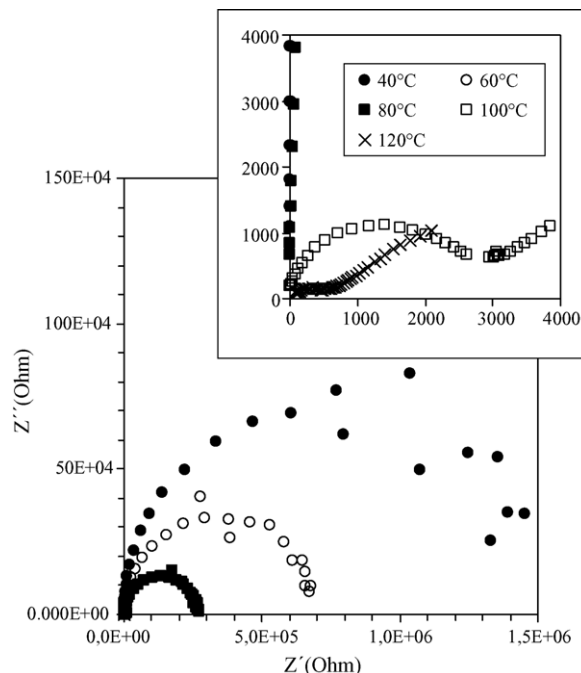


Fig. 4. Nyquist plots of a 100BTESB membrane sulfonated with the (CH₃)₃SiSO₃Cl solution at different temperatures. The high frequency region is shown in an expanded view.

Fig. 5 presents a plot of conductivity values as a function of temperature and relative humidity of the 100BTESB membranes sulfonated with HSO₃Cl and (CH₃)₃SiSO₃Cl solutions. The general trend observed is the increase of conductivity with temperature, although the values stabilize at temperatures around 100 °C. This behaviour 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. 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 mem-

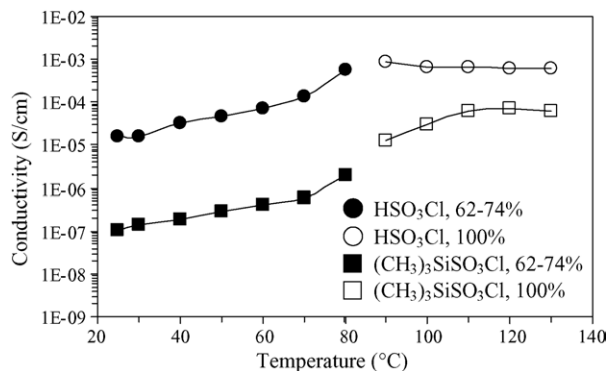


Fig. 5. Conductivity values as a function of temperature and relative humidity of the 100BTESB membranes sulfonated with HSO₃Cl and (CH₃)₃SiSO₃Cl solutions.

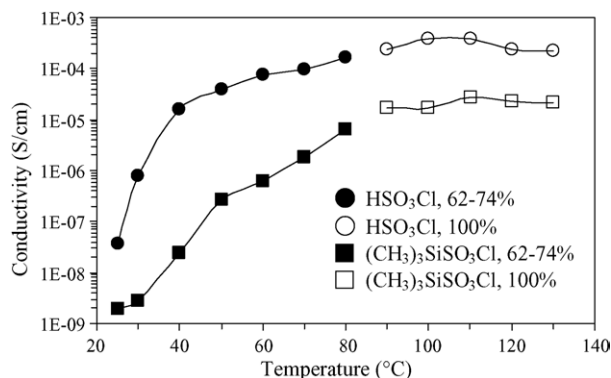


Fig. 6. Conductivity values as a function of temperature and relative humidity of the 50BTESB–50GPTMS membranes sulfonated with HSO₃Cl and (CH₃)₃SiSO₃Cl solutions.

brane with higher temperature. The behaviour of both membranes is similar, although the membrane sulfonated with HSO₃Cl solution presents conductivity values at low temperature two orders of magnitude higher than the membrane sulfonated with (CH₃)₃SiSO₃Cl solution. At higher temperature, this difference is reduced to one order of magnitude. The sulfonation process using HSO₃Cl solution is a more efficient method to attach SO₃[−] groups to aromatic rings due to its high reactivity compared with (CH₃)₃SiSO₃Cl. At higher temperature, the number of SO₃[−] groups is less important because of the high relative humidity and thermal activation moving nearer the effect of both sulfonating agents.

Conductivity values as a function of temperature and relative humidity of the 50BTESB–50GPTMS membranes sulfonated with HSO₃Cl and (CH₃)₃SiSO₃Cl solutions are shown in Fig. 6. The trends observed in this figure are similar to those of Fig. 5: increase of conductivity with temperature up to 90–100 °C and similar values above this temperature, and two orders of magnitude higher conductivities below 80 °C in the membrane sulfonated with HSO₃Cl solution. The main difference between both composition membranes is the maximum conductivity value reached, 8.5×10^{-4} and 3.9×10^{-4} S cm^{−1} for 100BTESB and 50BTESB–50GPTMS membranes, respectively. This small difference between membranes is showing that the incorporation of a higher organic content (with GPTMS) does not affect very much the proton conductivity at high temperature. At higher temperature, although the number of SO₃[−] groups is lower, the high relative humidity and thermal activation reduces this effect.

4. Conclusions

Organic/inorganic membranes using 1,4-bis(triethoxysilyl)benzene and (3-glycidoxypropyl)trimethoxysilane have been synthesised by polymerization of epoxy groups and inorganic condensation of silanol groups. Sulfonation pro-

cesses of aromatic rings to produce attached SO₃H groups together with a high porosity are necessary to provide proton conductivity. Thermal analysis shows a high water adsorption capacity when SO₃[−] and silanol groups are combined, and a reduction of the thermal stability at around 170 °C due to the decomposition of sulfonic acid groups. The chemical stability of the hybrid membranes to sulfonation process can be deduced by the absence of modifications in the FT-IR spectra. The measurement of conductivity by EIS shows a general increase with temperature, and stabilization at temperatures above 100 °C. This behaviour suggests the presence of two competing trends, one enhancing (thermal activation) and other reducing (dehydration) conductivity. The water retention properties provided by SO₃[−] and silanol groups leads to high proton conductivity (maximum values around 8.5×10^{-4} S cm^{−1}) at 100–150 °C.

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