Available online at www.sciencedirect.com

ScienceDirect

Journal of Membrane Science 307 (2008) 21–27

journal of MEMBRANE SCIENCE

www.elsevier.com/locate/memsci

Synthesis and characterization of P_2O_5–ZrO_2–SiO_2 membranes doped with tungstophosphoric acid (PWA) for applications in PEMFC

J. Mosa[a], G. Larramona[b], A. Durán[a], M. Aparicio[a,*]

[a] Instituto de Cerámica y Vidrio (CSIC), Campus de Cantoblanco, 28049 Madrid, Spain
[b] IMRA EUROPE, 220 rue Albert Caquot, BP 213, 06904 Sophia-Antipolis Cedex, France

Received 6 February 2007; received in revised form 15 June 2007; accepted 16 June 2007

Abstract

Homogeneous, transparent and crack-free P_2O_5–ZrO_2 and P_2O_5–ZrO_2–SiO_2 membranes have been synthesized by the sol–gel process. A first step has been oriented to the optimization of the synthesis and characterization of different compositions by TGA, FE-SEM, FTIR and EIS to choose the best inorganic composition in terms of chemical and mechanical stability, and proton conductivity. The addition of SiO_2 improves the mechanical and chemical stability. On the other hand, compositions with higher content in P_2O_5 have demonstrated lower mechanical and chemical stability against water, but higher proton conductivity. The water retention and high porosity of inorganic membranes leads to high proton conductivity, 10^{-2} S/cm, at 140 °C and 100% relative humidity. The second step has been focused in the study of doped inorganic membranes of molar composition $99.65(40P_2O_5–20ZrO_2–40SiO_2)–0.35PWA$. The high homogeneity, transparency and SEM-EDX analysis of these membranes indicates no phase separation suggesting that PWA is well dispersed in the inorganic structure. The incorporation of PWA in sol–gel oxides provides an increase of the proton conductivity at low relative humidity due to the adequate distribution of PWA in the inorganic network. Conductivity increases in two orders of magnitude at low humidity (10^{-4} S/cm at 50 °C and 62% RH) compared with undoped sol–gel oxide membranes.

Keywords: PEMFC; Sol–gel; Proton conductivity; PWA; Inorganic membrane

1. Introduction

Proton exchange membrane fuel cells (PEMFC) are extensively studied as one of the new energy conversion devices [1,2]. The currently developed PEMFC technology is based upon perfluorosulfonic acid membranes as electrolytes, such as Nafion®, which exhibits many attractive properties (high proton conductivity, good mechanical and chemical stability). Nafion® shows some shortcomings involving high cost, high methanol permeability and low conductivity under elevated temperature and low humidity conditions due to the loss of water [3–6]. To improve energy conversion efficiency and to avoid CO poisoning of catalysts, PEMFCs operating in the medium temperature range (100–200 °C) are strongly desired. Many efforts have been done to produce adequate proton-conducting membranes. In particular, inorganic membranes have been developed, such as gels derived of P_2O_5–ZrO_2 and SiO_2–P_2O_5–ZrO_2 systems [7–15].

The sol–gel method is an excellent process to produce proton-conducting materials because the gels contain a large number of micropores filled with liquid which can be used for fast proton transport. The sol–gel chemistry of phosphosilicates has been extensively studied, showing that the choice of the phosphorus molecular precursors plays a fundamental role in the characteristics of the final product, such as the extent of copolymerization between silicate and phosphate units. Phosphate esters react more slowly with water at ambient conditions in comparison with silicon alkoxides [16], whereas zirconium alkoxides reacts too fast and it is necessary their complexation to decrease hydrolysis rate [17].

Silicophosphate gels have shown to be fast proton-conducting solids. The mobility of protons increases when these are strongly hydrogen-bonded. Compared with Si–OH, phosphate glasses are more efficient for high proton conduction because the hydrogen ions are more strongly bounded to the non-bridging oxygen. Moreover, the hydrogen in the P–OH group is more

---

* Corresponding author. Tel.: +34 91 735 58 40; fax: +34 91 735 58 43.
E-mail address: maparicio@icv.csic.es (M. Aparicio).

0376-7388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2007.06.035

hydrogen-bonded with molecules, resulting in an increase in the temperature necessary to remove the water from P–OH. At the same time, the silicate network improves the mechanical strength and chemical durability while a high content in phosphorous decreases the chemical stability. The introduction of Zr^{4+} into silicophosphate gels also results in improved chemical stability [12]. Phosphotungstic acid, $H_3(P(W_3O_{10})_4)$ (PWA) is an interesting compound to be incorporated as dopant in sol–gel membranes to provide high proton conductivity [18–25]. These heteropoliacids can be used as inorganic modifiers because they have demonstrated to be highly conductive at low relative humidity and are thermally stable. The basic structural unit of PWA is the Keggin anion $(PW_{12}O_{40})^{3-}$ which consists of a central PO_4 tetrahedron surrounded by four W_3O_{13} sets linked together through oxygen atoms. They form 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. Hydrated PWA is known to present values at around 0.18 S/cm [19]. In spite of the promising initial results obtained using PWA in PEMFC membranes, the cell leakes some dissolved acid and performance decay. To overcome this problem, it would be interesting to block the PWA in the membrane by chemical bonding. The polyanion PWA clusters can be stabilized within the membrane through a strong coulombic interaction with an inorganic framework. If the assembled PWA is nanosegregated, the strongly acidic phase may originate an ionic conduction path with continuous channels [18,19].

In this work, we have prepared membranes with different compositions in the systems P_2O_5–ZrO_2 and P_2O_5–ZrO_2–SiO_2 using a sol–gel technique. SiO_2 was incorporated to the binary system looking for an improvement of the chemical stability of the materials. After a screening study, one composition was selected taking into account both, chemical stability and proton conductivity to be doped with PWA. The objective was to increase the proton conductivity of membranes, especially at high temperature and lower relative humidity, compared with undoped sol–gel oxides.

2. Experimental

Seven compositions have been studied in two different systems: P_2O_5–ZrO_2–SiO_2 and P_2O_5–ZrO_2. Table 1 shows the molar ratio of each composition. Membranes were produced by sol–gel using trimethyl phosphate $[PO(OCH_3)_3$, TMP] from Merck and zirconium tetrapropoxide $[Zr(OC_3H_7)_4$, TPZr] from Fluka for binary compositions, and also tetraethylorthosilicate $[Si(OC_2H_5)_4$, TEOS] from ABCR in the case of ternary compositions. Sols were prepared by mixing two solutions. The first one was prepared at room temperature by mixing TMP, TEOS (for ternary compositions), half the volume of propanol (solvent) (molar ratio of propanol/TEOS + TMP + TPZr = 2) and water as HCl 0.1N (molar ratio of water/TMP = 0.75 and water/TEOS = 1), stirring for 1 h. The second solution was prepared by mixing TPZr, the other half of propanol and acetylacetone (molar ratio of acetylacetone/TPZr = 1) stirring at room temperature for 1 h. Both solutions were subsequently mixed together for 10 min. The remaining amount of water as HCl 0.1N (total molar ratio of water/TEOS + TMP + TPZr = 3) was added drop by drop. The resulting homogenous and transparent solutions were stirred for 30 min. In the case of membranes doped with PWA from Fluka (99.65 oxides–0.35 PWA in molar ratio), the heteropolyacid was dissolved in the sol in the last step of the synthesis, after adding acidulated water.

Table 1
Molar ratios of compositions in systems P_2O_5–ZrO_2 and P_2O_5–ZrO_2–SiO_2

Composition	%P_2O_2	%ZrO_2	%SiO_2
1	50	50	–
2	60	40	–
3	80	20	–
4	25	25	50
5	35	35	30
6	40	20	40
7	60	30	10

Sols were cast in polytetrafluoroethylen (PTFE) and glass moulds, and left at room temperature and 50 °C in order to obtain homogeneous gels. The membranes were additionally treated at 150 °C in air for 2 h with a heating rate of 0.1 °C/min.

Thermal behavior of the membranes crushed to powder and previously dried at room temperature, 50 and 150 °C was studied by thermogravimetric analysis (TGA) in air up to 900 °C with a heating rate of 10 °C/min using a Netzsch STA 409. The fracture surfaces of the membranes were analyzed with a HITACHI S-4700 field emission scanning electron microscope (FE-SEM), and analysis by EDX (NORAN system six) was used to study the distribution of elements across the film thickness. Fourier transform infrared spectroscopy (FTIR Spectrum 100, Perkin-Elmer) was used to study the influence of incorporation of PWA in the oxide structure. FTIR spectra were recorded between 400 and 4000 cm^{-1} with a resolution of 2 cm^{-1}. The surface area was measured by the single-point N_2 adsorption method using a Monosorb Surface Area Analyser MS-13 (Quantachrome Co., USA). Proton conductivity was measured as a function of both relative humidity (RH) and temperature by electrochemical impedance spectroscopy (EIS) with a Gamry FAS2 from 1 Hz to 1 MHz. Two parallel silver electrodes were painted on both sides of the transparent films. The measurements were made at lab conditions (25 °C, 35–40% RH), and allowing samples to equilibrate at different RH for 24 h inside a sealed cell containing saturated solutions of $Ca(NO_3)_2$ (24–100%), $NaNO_3$ (62–100%) and KNO_3 (90–100%). Temperature and relative humidity have been measured using a Rotronic HYGROCLIP HK 25.

3. Results and discussion

Transparent and yellowish glass-like gels were obtained in all the cases after drying at 50 °C and further treatment at 150 °C. For ternary system, gelling time is much shorter that in binary systems because the incorporation of SiO_2 (glass former) makes the network development easier. Gelling time changed from 5 to 1 day for silica contents of 10 and 50%, respectively.