Mesoporous α-Fe$_2$O$_3$ membranes as proton conductors: Synthesis by microwave-assisted sol–gel route and effect of their textural characteristics on water uptake and proton conductivity

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ABSTRACT

This paper reports novel inorganic proton exchange electrolytes based on mesoporous α-Fe$_2$O$_3$ ceramic membranes. The unsupported mesoporous hematite proton ceramic membranes with high specific surface areas, high pore volumes, and narrow pore size distributions have been synthesized from a hydrolytic ferric oxide polymer prepared by a microwave-assisted sol–gel route. The effect of their textural characteristics on water uptake and proton conductivity has been studied.

Microwave heating allows us to obtain homogeneous hydrosols at short times (2 s) meanwhile conventional heating gives rise to inhomogeneities in the hydrosol independently of heating times. Electron diffraction TEM observations show that the xerogels calcined at 200 °C are polycrystalline in nature and correspond to α-Fe$_2$O$_3$ in accordance with the two characteristic vibrations in hematite observed by FTIR spectroscopy. According to EMF measurements, proton transport is observed in these ceramic membranes and shows an Arrhenius dependence on temperature for all relative humidities studied. A sigmoidal dependence of the water uptake and the proton conductivity with the RH at a constant temperature was observed with the greatest increase detected between 58% and 81% RH. The pore volume and the average pore size of the α-Fe$_2$O$_3$ mesoporous ceramic membranes seem to be the main factors which influence the water uptake and consequently the proton conductivity in the studied ranges. The membranes with the largest pore volume, and the largest pore size have the highest water uptake and in turn the highest values of proton conductivity in the whole range of relative humidities (RHs). According to the activation energy values, proton migration in this kind of materials could be dominated by the Grotthuss mechanism in the whole range of RH.

1. Introduction

Nowadays hematite is used either as finely divided powders or as porous solids with a high ratio of surface area to volume. In fact, they are widely employed as red pigments, catalysts in dehydrogenation reactions, photocatalyst used in UV light activated processes, anticorrosive agents, starting materials in the synthesis of magnetic ferrites, in nonlinear optics, gas sensors and magnetic applications [1–7]. In addition, it has been intensively investigated as electrode in high rate rechargeable lithium batteries [8,9].

Mesoporous ferric oxide ceramic membranes could be suitable as electrolytes in proton exchange membrane fuel cells (PEMFCs). For that application, future materials should provide high proton conductivity at low temperature; they should be hydrophilic and mechanically, thermally, and chemically stable; they also should be impermeable to H$_2$ and O$_2$. Sol–gel processing offers the possi-

bility to obtain tailored porosity and pore size, controllable surface chemistry and structural and mechanical integrity. Thus, the synthesis of iron oxides with nanoporosity is a matter of great interest since is expected that hematite exhibits proton conductivity.

Traditionally, iron (III) oxides have been prepared by hydrolysis and precipitation from aqueous solutions of Fe (III) salts [10]. Either heating or addition of base has been shown to induce the formation of iron (III) oxide gels from such solutions. Usually, the hydrolysis and condensation of Fe (III) species is so rapid that gelatinous precipitates are the exclusive products of such synthesis. In order to avoid the precipitation of the iron (III) oxides several reports of sol–gel synthesis approaches have been published [10–13]. In general, these sol–gel syntheses consist of the addition of organic polydentate ligands to a solution of an Fe (III) salt followed by heating on the solution. However, in those syntheses organic media are employed. On the contrary, we have chosen aqueous media for the synthesis reported here since it is an environmentally friendly process.

In addition, microwave irradiation has shown a great potential for the synthesis and processing of ceramic materials. In particular,

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microwave-assisted hydrothermal synthesis has dominated the preparation of nanopowder iron oxides [14–18]. However, the same cannot be said with respect to the combination of the sol–gel processes with the microwave irradiation. That irradiation can accelerate condensation reactions that can confer a harder but a more flexible polymer and thus to lead a better structural and mechanical integrity. For those reasons together with the possibility to tailor pore volume and pore size, microwave assisted sol–gel technique is considered in this study.

This paper reports novel inorganic proton exchange membranes based on mesoporous α-Fe_2O_3 ceramic membranes that could be used as electrolytes in PEMFCs, as it is mentioned above. At present, Nafion is one of the few materials that deliver the set of chemical, electrochemical and mechanical properties required to perform as a good electrolyte in PEMFCs [19]. However, Nafion® membranes are very expensive, hard to synthesize and present environmental problems with regard to recycling and disposal of fluorinated polymers and their separation from the platinum catalysts used. In addition, polymer and hybrid membranes are susceptible to deformation on the basis of their repetition of sorption, desorption, and permeation of water. The deformation increases the interfacial resistance between the membrane and electrodes, and decreases the fuel cell performance. Moreover, the detrimental problem for high temperature use of Nafion is the loss of grafted HSO_4 branches, the large in-homogeneity in the groups distribution resulting from the anchoring starting at the pore mouths, as well as the loss of its good mechanical properties [20]. Although, the two first problems can be solved employing a "co-condensation" process of sodium metasilicate with (3-mercaptopropyl)-trimethoxysilane (MPMS) as a sulfur-containing silica source, since higher values and more homogeneous distributions of conducting groups per square nanometer can be reached [21], the third problem keeps unsolved.

Over the last 10 years, the proton conductivity characteristics of porous P_2O_5–SiO_2 glasses, xerogels, ceramic membranes, solid acids, and ordered mesoporous silica membranes have been the subject of growing interest due to their potential as solid electrolytes in sensors, fuel cells, etc [22–35]. However, the application of solid acids as electrolytes in a fuel cell requires lower thicknesses than they show, i.e., 1.5 mm [34]. In addition, a subsequent study has indicated that this type of materials may be not stable in fuel cell environments [35]. The same problem of instability affects to the glasses based on phosphates [23]. Ordered mesoporous MCM-41 silica with assembled $H_3PW_{12}O_{40}$ nanoparticles by the vacuum-assisted impregnation method have been prepared and showed proton conductivity values of 1.8×10^{-2} and 4.5×10^{-2} S/cm at 25 and 150 °C, respectively. However, a drastic and rapid decrease in conductivity occurs as a function of time due to a partial or a total loss of the impregnated acid [36].

The synthesis of mesoporous α-Fe_2O_3 ceramic membranes from a hydrolytic ferric oxide polymer prepared by a microwave-assisted sol–gel route in aqueous media is described. Electromotive force (EMF) measurements were performed to determine the type of carrier responsible of the conduction process. In addition, studies on water uptake and on the electrical conductivity of two membranes with different textural characteristics as a function of both temperature and relative humidity are also reported. This study aims at establishing the relationships between their textural characteristics and their water uptake and transport properties.

2. Experimental

2.1. Synthesis of the mesoporous membranes

Membrane preparation begins with the synthesis of an electrostatically stabilized hydrosol by the hydrolysis of a ferric salt

solution. The product species depends on the physicochemical conditions of the reaction (e.g. precursors, concentration, temperature, pH). In this study, the spherical hydrolytic polymer [Fe(O,O-H,OH₂)₆]ₙ was used as colloidal precursor. The cationic hydrolytic ferric oxide polymer was prepared by weak-base ($NaHCO_3$) titration of a 2 M fresh ferric nitrate solution. Equal volumes of titrant and nitrate solution were used to optimize mixing and reduce local precipitation. The $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in Milli-Q water and it was then filtered through 0.2 µm nucleopore filter and placed in a 250 ml Pyrex reaction flask. The $NaHCO_3$ was dissolved in Milli-Q water using an ultrasonic bath. This solution was then titrated at a rate of 2.5 ml/min. into the rapidly stirred iron solution. The solution turned red after about 15 min. It was stirred for 1 more hour after the titration was finished. The hydrolytic solution was placed in a Teflon bottle at 100 °C for 2 min in a microwave furnace (Perkin–Elmer Multiwave 2000 system, Waltham, MA, USA), and then quenched in ice-water. For comparison, a conventional heating was also employed using a conventional furnace (Nabertherm GmbH P330, Lilienthal/Bremen, Germany) at the same temperature. The hydrosols were dialyzed in a 3000 MWCO membrane against Milli-Q water until the pH was 4.0. The solution was then concentrated by rotary vaporization until a 0.62 M [Fe^{III}] sol was obtained. Monolithic xerogels were prepared from approximately 10 ml aliquots of concentrated hydrosol by slow evaporation in a polystyrene container at room temperature and controlled humidity conditions (33% R.H. over a saturated solution of $MgCl_2 \cdot 6H_2O$). After drying, the xerogels were washed with deionized water and then were fired in air at different temperatures (200, 250, and 300 °C) for 1 h and a cooling and a heating rate of 2 °C/min in each case. Porosity in the xerogels is generated from interparticle pores. No templates were used during either the synthesis or the drying processes. For the possible application considered in this study, electrolyte in a PEMFC, the porosity should have a certain tortuosity since H_2 should not permeate through the membrane. Mesoporous materials like MCM membranes with ordered porosity are more open structures and undesirable H_2 permeability can occur more easily than in a structure with porosity from interparticle pores, i.e., with a certain tortuosity.

The effect of heating on textural characteristics, crystallinity, phase transitions and on microstrutural development of the membranes have been studied.

2.2. Structural characterization techniques, XRD, FTIR, TEM and XPS studies

X-ray diffraction was conducted on a Scintag 4-circle X-ray diffractometer with a CuKα target. The identification was made using the Powder Diffraction File, which was included in the program employed and using the Scherrer's equation [37] the crystal size (S) was calculated:

$$S = \frac{K\lambda}{\beta \cos \theta} \tag{1}$$

where K is the shape factor (0.9), λ is the X–ray wavelength (CuKα₁ = 1.54060 Å), β is the full width at half maximum intensity (FWHM) in radians, and θ is the Bragg angle in degrees.

FTIR spectroscopy (Perkin–Elmer 1330 spectrophotometer with a 3600 data station) was performed on KBr pellets of powdered membranes. The ceramic membranes were also characterized by transmission electron microscopy (TEM) (JEOL JEM 2000FX, working at 200 kV, Japan) and high-resolution transmission electron microscopy (HR-TEM), (JEOL JEM 3000F, working at 300 kV, Japan), respectively. Selected area electron diffraction (SAED) patterns studies were performed with the above mentioned microscopes Local composition was analyzed by energy dispersive of X-ray