

PROTONIC CONDUCTORS FOR PROTON EXCHANGE MEMBRANE FUEL CELLS: AN OVERVIEW

At present, Nafion, which is a perfluorinated polymer, is one of the few materials that deliver the set of chemical and mechanical properties required to perform as a good electrolyte in proton exchange membrane fuel cells (PEMFCs). However, Nafion presents some disadvantages, such as limiting the operational temperature of the fuel system (80°C), because of its inability to retain water at higher temperatures and also suffers chemical crossover. In addition to these restrictions, Nafion membranes are very expensive.

Reducing costs and using environmentally friendly materials are good reasons to make a research effort in this field in order to achieve similar or even better fuel-cell performances. Glass materials of the ternary system $\text{SiO}_2\text{-ZrO}_2\text{-P}_2\text{O}_5$, hybrid materials based on Nafion, and, nanopore ceramic membranes based on SiO_2 , TiO_2 , Al_2O_3 , etc. are considered, at present, as promising candidates to replace Nafion as the electrolyte in PEMFCs. These types of materials are generally prepared by sol-gel processes in order to tailor their channel-porous structure and pore size.

In this communication, the possible candidates in the near future as electrolytes (including other polymers different than Nafion) in PEMFCs are briefly reviewed. Their preparation methods, their electrical transport properties and conduction mechanisms are considered. The advantages and disadvantages of these materials with respect to Nafion are also discussed.

Fuel cells are being developed for use in stationary, transportation and portable devices, owing to their inherently high-energy efficiency and ultra low or zero emission of environmental pollutants, compared to the internal combustion engine.

In a recent review on fuel cell systems, Steele [1] reported that the General Electric Company (USA) initiated development of solid polymer electrolyte fuel cells in the 1950's for the Gemini space capsules. Although high Pt loadings were used with a polystyrene sulphonate ion exchange membrane incorporated in these systems, the power densities were relatively low. However, the introduction of the superior perfluorinated sulphonic acid polymer, Nafion, in the 1960's ensured that development of polymeric electrolyte fuel cells continued. Unfortunately, Pt loading was still too high in 1970, and investigations into protonic exchange membrane fuel cells (PEMFCs) systems almost disappeared for more than a decade until Ballard (Canada) began work in 1984 under a contract from the Canadian Defense Department. By the mid 1990's Ballard had overcome many of the engineering problems associated with this system, and were able to demonstrate high power density loadings in 1 kW stack (1.5 W/cm^2 with low Pt (0.5 mg/cm^2) [2].

Several advances in PEMFCs have been made including the reduction of the quantity of platinum electrode catalyst needed, and membranes with higher specific conductivity, good water retention and long lifetimes [3]. A major limitation of the current PEMFCs is that the Pt anode electrocatalyst is poisoned by CO at the 5 to 10 ppm level in fuel cells operating at about 80°C. CO tolerant electrocatalysts (e.g., Pt-Mo, Pt-Ru) have been investigated to enhance CO tolerance, but the problems with these electrocatalysts are that (i) the Pt loading is 5 to 10 times higher than required for pure

platinum catalysts and (ii) their CO tolerance level is about 50 ppm and even, at this level, this leads to an increased overpotential for the anodic reaction [4,5].

The current PEM fuel cells are also complicated by the issue of water management. For example, the proton conductivity of the PEMFC increases linearly with the water content of the membrane, with the highest conductivity corresponding to a fully hydrated membrane. It would be desirable to operate a fuel cell at a temperature above the boiling point of water from the standpoint of increased reaction kinetics and lower susceptibility to CO poisoning; however, with increasing temperature the membrane loses conductivity due to drying. Membrane dehydration also causes the membrane to shrink, which reduces the contact between the electrode and membrane, and may also form pinholes leading to the crossover of the reactant gases.

To solve both the CO poisoning and water-thermal management problems, the present state-of-the-art proton exchange membranes need to be modified in order to remain hydrated at higher operating temperatures than for the current PEMFCs.

At present, Nafion is still used as electrolyte in PEMFCs because, is the best material that fulfils the requirements needed in this type of fuel cell. However, other materials are currently being studied in order to replace Nafion as electrolyte in PEMFCs and direct methanol fuel cells (DMFCs).

The objective of this overview is to describe briefly the state-of-the-art of protonic conductors for low temperature fuel cells (up to 130°C) as possible candidates as alternative electrolytes in PEMFCs.

NAFION AND OTHER MEMBRANE POLYMER ALTERNATIVES

As mentioned above, Nafion is used nowadays as electrolyte in PEMFCs. This polymer is made of a perfluorocarbon sulfonic acid ionomer, which is still the electrolyte against which others are judged, and is in a sense an "industry standard". Nafion is based on

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the microstructures. The less pronounced hydrophobic/hydrophilic separation of sulfonated polyetherketones compared to Nafion corresponds narrower, less connected hydrophilic channels and to larger separations between the less acidic sulfonic acid functional groups. This leads to a disadvantageous swelling behaviour and a stronger decrease of water and proton transport coefficients with decreasing water content; however, the hydrodynamic flow of water, i.e., electroosmotic drag and water permeation, is reduced compared to Nafion, which is an essential advantage, especially for DMFC applications.

Polymers based on sulfonate PEEK are not only interesting, low-cost alternative membrane materials for hydrogen fuel-cell applications, but may also help to reduce the problems associated with high water drag and high methanol crossover in DMFCs. The relatively high conductivities (slightly lower conductivity than that of Nafion) observed for oligomers containing imidazole as functional groups may be exploited in fully polymeric proton conducting systems, with no volatile proton solvent operating at temperatures significantly higher than 100°C, where methanol vapour may be used as a fuel in DMFCs.

Buchi et al. [16] reported the preparation of proton exchange membranes by the synthesis of pre-irradiation grafting of styrene/divinylbenzene mixtures into poly(fluoroethylene-co-hexafluoropropylene) films and subsequent sulfonation. The problem of shaping is overcome as a result of the grafted polymer process. This is a potentially cheap and easy technique for the preparation of solid polymer electrolytes [16].

López et al. [17] reported the preparation of new, cation-exchange membranes from polymer composites based on poly(vinylidene fluoride), sulfonated polystyrene-co-divinylbenzene and antimoniac acid. Values of the transport number of protons in the membranes were obtained from the observable electric potential, which is defined as the potential difference measured between the electrodes reversible to one of the constituent ions in equilibrium with the system. When compared with Nafion cation-exchange membranes, the membranes described in this work exhibited interesting proton-transport properties that could make them suitable as polymer electrolytes in fuel cells. The authors claimed that the conductivity of their polymers based on Poly(vinylidene fluoride) equilibrated with a 1M HCl solution and at 25°C showed a conductivity value of 0.09 S/cm. This value is higher than that of Nafion under the same measurement conditions, but the electrical behaviour was not characterized at higher temperatures. Dehydration problems are unknown in these polymers at the operation temperature of a cell. However, the authors do not measure the performance of their polymers as electrolytes in PEMFCs.

The impregnation of polymers bearing oxygen or nitrogen donor centers in strong acids like H₃PO₄ or H₂SO₄ led to the formation of proton-conducting

materials [18]. A series of polymers like PEO, polyamides, polyamines such as poly(2-vinylpyridine) P2VP, poly(4-vinylpyridine) P4VP, poly(ethyleneimines) have been investigated for their potential use as polymer electrolytes when they are doped with a strong acid. Polybenzimidazole (PBI) doped with H₃PO₄ 85% was also proposed for operation at temperatures up to 200°C [18]. This polymer exhibits good proton conductivity, excellent thermal stability and moderate mechanical strength at elevated temperatures. To improve the performances of "high temperatures" proton-conducting polymers, Deimede et al. [19] have recently combined the good conductivity and superior mechanical properties of sulfonated polysulfone (SPSF) with the very good conductivity of PBI resulting thus in polymeric membranes, which after doping with H₃PO₄ form proton conducting polymeric electrolytes.

Although a great effort is being conducted in the search for novel polymers that can be used as electrolytes in PEMFCs, Nafion is still the best polymer at present that accomplishes the requirements needed as electrolyte in PEMFCs.

Another important problem to consider is that polymers cause an environmental damage (synthesis and recycling).

Other possible candidates to replace Nafion in the future, apart from the polymer materials, are:

Silicate-phosphate glasses [20], hybrid materials based on Nafion [21] and nanopore ceramic membranes such as high porosity silica or TiO₂ (anatase) membranes [22]. All of them, except the hybrid materials are environmentally friendly materials.

GLASSES AS PROTON CONDUCTORS

Oxide glass conductors are divided into two types: alkali-ion conductors and electronic conductors containing transition metal oxides. Abe et al. [20], have reported silicate phosphate glasses, free of alkali, with high electrical proton conductivity, compared with silicate glasses. The hydroxyl groups in these glasses are strongly bonded with the counter oxygen, and a high proton concentration with strong hydrogen bonding (mobile protons). The content of protons in glasses decreases with increasing glass melting temperature. Therefore, it is necessary to prepare the glass with a large concentration of protons at low temperatures, that is the say, by using the sol-gel technique. It was surprising that the conductivity of the glasses was much higher than those glasses containing protons, but not molecular water. Abe et al. [23] proposed a mechanism for proton conduction in the sol-gel derived glasses, in which, the dissociated protons (by means of an electrical field) move through molecular water so that the activation energy for proton transport is smaller than that in glasses containing no molecular water. These authors [23] indicated that protons are bound with oxygen to form hydroxyl groups,

which are in turn bounded attaching to network forming cations such as Si^{4+} and P^{5+} .

Nogami and Abe [24] studied the effect of molecular water on proton conduction from conductivity measurements of silica glasses, with and without water molecules. These studies indicated that the electrical-conduction process is rate-controlled by dissociation of protons from OH and H_2O , and the activation energy decreases with the logarithm of the product of $[\text{H}^+]$ and $[\text{H}_2\text{O}]$.

Nogami et al. [25], prepared fast proton-conducting glasses based on $\text{P}_2\text{O}_5\text{-ZrO}_2\text{-SiO}_2$ using the sol-gel method and constructed for the first time, a hydrogen concentration cell using a glass as electrolyte. The gel prepared is porous and contains water and solvents incorporated during gel synthesis. Upon heating, the gel releases the water and solvents and shrinks due to the hydration-condensation of the hydroxyl group. The porous structure remains unchanged in glass when heated below 900°C . Silicate phosphate porous glasses, obtained by heating a gel at 700°C , had a specific surface area of $250\text{ m}^2/\text{g}$ and exhibited room temperature conductivities of 6×10^{-5} and $2 \times 10^{-2}\text{ S/cm}$ under 0.54 and 0.9 water-vapor pressure, respectively.

These high conductivities are regarded as fast protons conductors accelerated by molecular water bonded to POH groups. The hydrogen concentration cell, where the glasses were used as electrolyte, showed a Nernstian response to hydrogen pressure.

Nogami et al. [26] showed that $\text{P}_2\text{O}_5\text{-SiO}_2$ binary glass could be prepared by the sol-gel method using $\text{PO}(\text{OCH}_3)_3$ and $\text{Si}(\text{OC}_2\text{H}_5)_4$. The surface area and the pore volume of the glass obtained by heating at 700°C was $488\text{ m}^2/\text{g}$ and $0.37\text{ cm}^3/\text{g}$, respectively. Pore diameters in the sample were less than 5 nm with an average diameter of 3 nm. The solid state proton nuclear magnetic resonance (PNMR) spectrum of the glass indicated that phosphorous ions are not polymerized but are bound with the silicon-oxygen tetrahedra or hydroxyl groups. In the infrared (IR) spectrum of the as-prepared glasses, a band assigned to the hydrogen-bond-free Si-OH bonds and bands corresponding to P-OH bonds were found.

According to these authors [26], the glass exhibited a conductivity of $2.2 \times 10^{-2}\text{ S/cm}$ at 50°C and 70% R.H. and can function as a proton fuel-cell electrolyte. This is the highest conductivity obtained in this type of glass. The activation energy was calculated to be $\sim 5\text{ kJ/mol}$, and is related to the energy necessary for the dissociation of a proton from the hydroxyl groups (see figure 2). These fast proton-conducting glasses could act as substitute for perfluorinated ionomers. Nogami et al. [26] also constructed a $\text{H}_2\text{-O}_2$ fuel cell. The polarisation curve is plotted in figure 3; the power output was about 6 mW/cm^2 , which is one or two orders of magnitude smaller than that using polymer

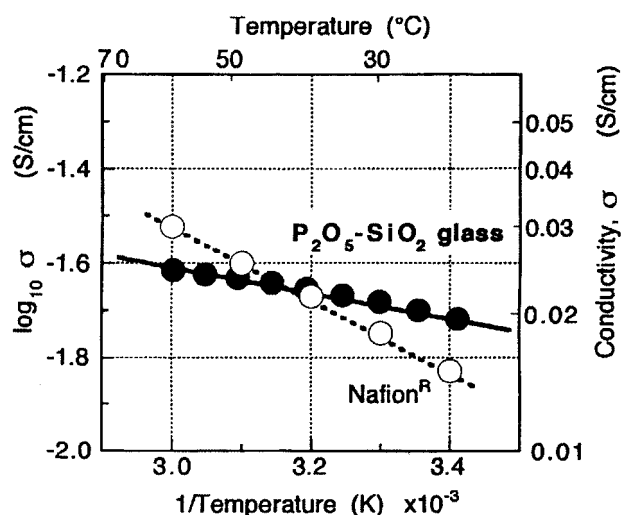


Figure 2. Glasses and Nafion Conductivities comparison according to Nogami et al. [26].

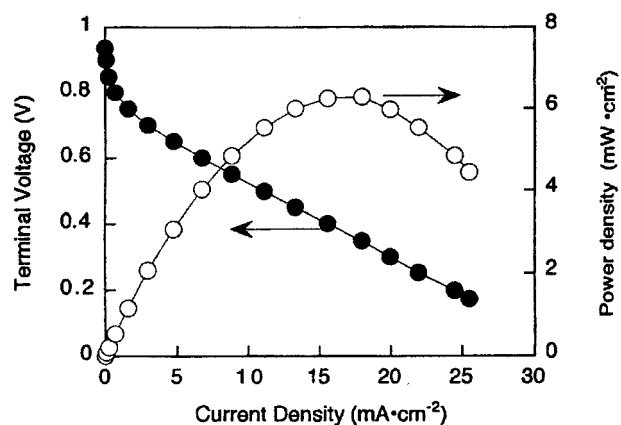


Figure 3. Polarisation curve of glasses according to Nogami et al. [26].

membranes. However, these authors [26] claimed that, this high power level for a polymer membrane is the fruit of research efforts over the past 30 years, since the first discovery. These authors suggested that the output power can be increased by optimizing the electrode and sample size.

Nishiwaki et al. [27] prepared surfactant-templated mesoporous silica gel impregnated with various protonic acids. A sol-gel process was used to prepare the silica-surfactant nanocomposite. The conductivity of the mesoporous silica gel impregnated with 5.0 M H_2SO_4 was $\sim 1 \times 10^{-4}\text{ S/cm}$ at room temperature in a dry nitrogen-gas atmosphere. These authors did not measure their gels at high relative humidities. At high RH those gels could have higher proton conductivity.

Glasses with a high concentration of molecular water are promising candidates to replace Nafion. However, it is desirable to make an effort to enhance their low chemical durability in atmospheres with high

water vapour partial pressure. This problem would affect a long life time of the fuel cell.

It is important, therefore, to understand how molecular water affects proton conduction and to design glasses with highly effective molecular water determine a truly effective molecular water for the development of high-proton conducting glasses.

ORGANIC-INORGANIC HYBRID MATERIALS

A hybrid material is a composite material constituted of an organic polymer and an inorganic material. Two types of hybrid materials can be distinguished: Type I, which corresponds to hybrid materials where the organic molecules or polymers of low molecular weight are imbibed in an inorganic matrix, and type II that corresponds to hybrid materials in which the organic and the inorganic components are joined by covalent or ionic-covalent bonds (both networks are simultaneously or sequentially formed). In the first case, hybrid materials of type I, the interaction between the organic and the inorganic components are weak, i.e., of the Van der Waals type, whereas in the second case, the interaction is at a molecular level. [28–30]. Some hybrid materials have been synthesized and electrically characterized to establish if they can be used as electrolytes in PEMFCs.

Watanabe et al. [21] dealt to overcome the management of water in the electrolyte, one of the most complicated problems in PEMFCs. These authors tried to prepare a Nafion self-humidifying system, which consisted of the electrolyte of 50 mm Nafion membrane containing 0.07 mg/cm^2 of platinum catalyst particles ($d = 1$ to 2 nm) and a few weight percent of a hygroscopic material, such as silica or titania ($d = 5$ to 7 nm). The platinum particle catalyzes the oxidation of crossover hydrogen to generate water, which in turn is adsorbed by the oxide particles. The cell showed exceptionally stable and high performance even under conditions of ambient pressures when operated with hydrogen saturated with water at 20°C and dry oxygen. The internal resistance was measured to be $0.06 \Omega\cdot\text{cm}^2$, and the output of the cell was 0.63 W/cm^2 , i.e. 0.9 A/cm^2 at 0.7 volts with an energy efficiency of 60%. The output was 1 W/cm^2 in the voltage region of 0.6 to 0.4 , yielding a current density of 1.6 to 2.5 A/cm^2 . Hydrogen depleted for self-humidification was estimated to be less than a few percent under these operating conditions.

There have been previous efforts to enhance the water retention of Nafion and related membranes by incorporation of hydrophilic metal oxides (e.g. SiO_2). Difficulties have been encountered because the metal-oxide particles are micron size and are not sufficiently small to enter the nanopore structure of the membrane [31]. To overcome this problem other authors used a sol-gel technique to introduce a polymeric form of oxide, into the perfluorosulfonic acid. Using this

method, it was shown that the oxides enter the fine channels ($\sim 5 \text{ nm}$ in diameter) [32].

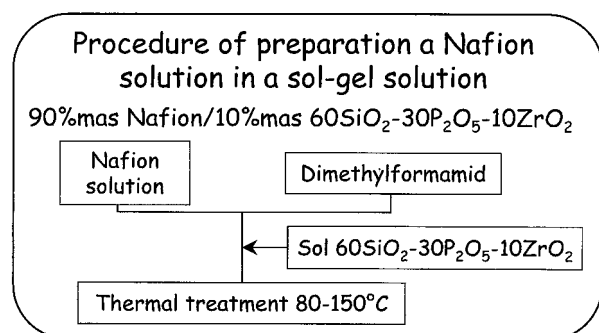
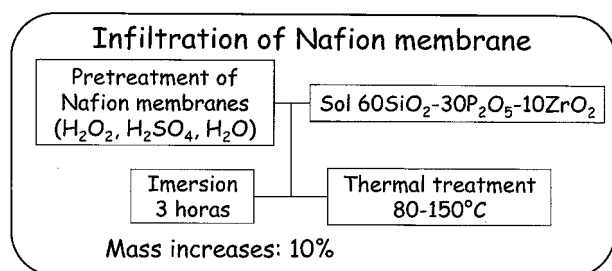
To enhance the proton conductivity of ion-exchange membranes at elevated temperatures by incorporating Nafion with sol-gel processed to silicophosphates. These gels were designed to provide a high concentration of protons by tying up the water in the pores and reducing its volatility [33].

Aparicio et al. [34] prepared composite membranes by impregnation of NafionTM with a $\text{SiO}_2\text{-P}_2\text{O}_5\text{-ZrO}_2$ sol. The incorporation of $\text{SiO}_2\text{-P}_2\text{O}_5\text{-ZrO}_2$ provided a significant increase in water retention capabilities for Nafion, allowing the composite membranes to be operated at elevated temperature (130°C). The infiltrated membrane treated at 150°C showed better performance, compared to a sample treated at 80°C , due to a higher hydroxyl-group content. In addition, composite membranes were less susceptible loss of proton conductivity at high temperature than unmodified Nafion. The total weight increment was 10% and Nafion content was 90% wt. An organic compound was also incorporated in order to increase the sol absorption into Nafion; the heat treatment of the hybrid infiltration membrane was between 80° and 150°C . After the heat treatment of the membrane, TGA, DTA and SEM characterisation techniques demonstrated that the posttreated and infiltrated Nafion maintains its mechanical and structural properties, and the OH group concentration and stability is greater at temperatures as high as 150°C . The polarisation curve (Figure 4) indicated excellent performance, for the infiltrated Nafion, at 150°C , as electrolyte in a chemical cell constructed as $\text{H}_2(130^\circ\text{C}) / \text{Cell}(130^\circ\text{C}) / \text{O}_2(130^\circ\text{C})$.

However, a study of higher duration is needed in order to know if the stability of the hybrid membranes is adequate.

Bermudez et al. [35], reported organic-inorganic hybrids prepared by the sol-gel process, which were investigated by infrared spectroscopy at room temperature. The matrix of the so-called ureasils is a silica network to which oligopolyoxyethylene chains are grafted by means of urea cross-links. The ureasils prepared-U(2000), U(900), and U(600)-are obtained by reacting three diamines (containing about 40.5, 15.5, and 8.5 oxyethylene units, respectively) with 3-isocyanatepropyltriethoxysilane. Spectroscopic data reveal that the number of oxyethylene units present dramatically affects the amide I and amide II bands and indicate that the N-H groups of the urea linkage are involved in hydrogen bonds of different strength. The existence of non-hydrogen-bonded urea groups and hydrogen-bonded urea-urea and urea-polyether associations is suggested. The conductivity for these hybrid materials is also fairly low for PEMFCs. The knowledge of the textural properties of such polymers is

Preparation of Nafion/dry silicophosphates sol-gel



Characterization TGA, DTA, SEM, EDS, XRD, Pore analysis, EIS

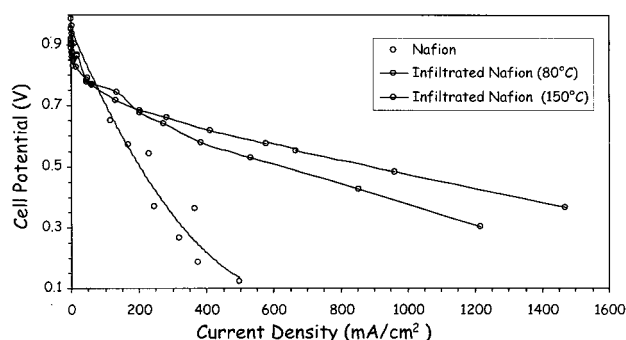


Figure 4. Polarisation curves of hybrid materials according to Aparicio et al. [34].

necessary in order to establish why the proton conductivity is lower than that of Nafion.

Hybrid materials can combine different properties of both inorganic and organic materials but still have the problem that they are not environmentally friendly materials.

POROUS CERAMIC MEMBRANES

Nano-particle production using the sol-gel method represents an attractive approach for fabricating xerogels and ceramic materials with a pore size close to the molecular level (about 2 nm in diameter or slightly higher). In the particulate sol-gel process, the diameter of the resulting pores in the xerogels and resulting ceramics is a function of the primary particle size in the

precursor sols, the configuration and packing geometry of the particles, and the thermal history of the sample during subsequent sintering steps. The ideal pore structure can be obtained only when one controls every step in the process. It is generally accepted that in the sol-gel process, for silica synthesis from alkylsilicates, spherical colloids are formed under base catalyzed systems having higher water:alkyl silicate ratios (r) [36,37].

Gelation of colloidal suspensions can be achieved either via evaporation of solvent from the sols or through the gradual removal of charge-determining ions from the sols. These two different methods of destabilizing a sol result in different packing densities of particles and different gel structures. The former method promotes dense packing, while the latter produces a loose packing structure. The latter method is based on charge neutralization by gradually removing charge-determining protons from the sol. In this case, the charge density on the particle surfaces decreases gradually leading to aggregation. Since this process proceeds slowly, a spongy type of aggregate, or agglomerate, is produced. These agglomerates grow with the continuous withdrawal of charge from the particle surfaces until gelation occurs. The dialysis technique has been used to facilitate this charge-removal process. Since the pH of the suspension determines surface charge density for metal oxide particles, a shift in pH towards the isoelectric point (IEP) produces this type of agglomerate and yields a gel with an open structure.

Furthermore, by means of the dialysis technique, the organic solvent (ethanol in the case of TEOS hydrolysis) formed during the polycondensation reactions, are removed at room temperature.

Compared to polymeric sol-gel routes, sol-gel processing of particles offers a sharper pore-size distribution in the final product.

Colomer and Anderson [38] prepared both micro and micro and mesoporous SiO₂ xerogels of high porosity, high specific surface area and small pore size (up to 10 nm) by a particulate sol-gel route with a water:TEOS molar ratio, $r = 83$. The main objective of their work was to design micro and micro and mesoporous SiO₂ stable structures, with the aim of obtaining proton exchange electrolytes. A preliminary study of the electrical conductivity of some xerogels with different structural characteristics as a function of both temperature and relative humidity was reported. A hydrogen concentration cell, where these silica xerogels were used as the electrolyte, showed a Nernstian response to hydrogen pressure. Protons are the mobile specie in this type of material (Figure 5). A modification of the surface site density of the xerogels (number of water molecules per square nanometer), enhances their electrical conductivity. When silica xerogel were treated at pH 1.5, their proton conductivity increased from 2.84×10^{-3} to 4.0×10^{-3} S/cm at 81% RH and 80°C, indicating that the surface-site density has a significant effect on conductivity.

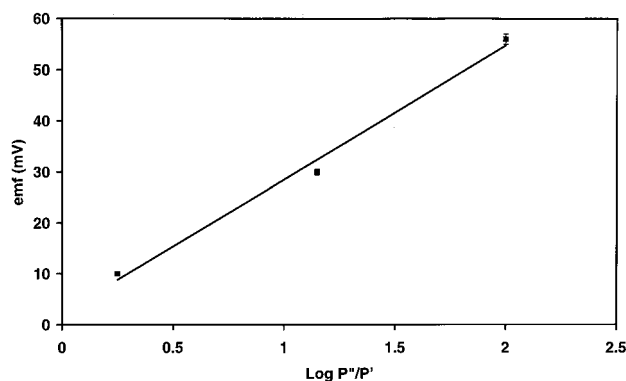


Figure 5. Relationship between emf and relative hydrogen gas pressure at room temperature and 81% RH, according to Colomer and Anderson [38].

The ability of these materials to retain water at different temperatures has been studied at different temperatures by thermogravimetric analysis (TGA). Data extracted from the TG curves of the hydrated metal oxide xerogels and Nafion under 81% RH showed that the thermal stability of the physisorbed water is similar for the ceramic membranes (76–85°C) and lower for Nafion (60°C). The number of water molecules per square nanometer varies between 22 for SiO₂ to 64 for TiO₂ [22]. There are literature data on the state of hydration of Nafion in terms of mmol_{H₂O}/cm³. This value permits a more direct comparison with the porous metal-oxide ceramics. Under the above-mentioned experimental conditions, TiO₂ and Al₂O₃ showed the highest water content per unit volume (26 and 25 mmol/cm³, respectively), followed by SiO₂ (20 mmol/cm³) and finally Nafion (18 mmol/cm³). The proton conductivity value did not correlate with the water content of a sample. This indicates that differences in both proton concentrations and proton mobility in the pore wall exist.

Vichi et al. [22] showed that the proton conductivity had a pronounced dependence with relative humidity; for γ -Al₂O₃ this dependence is linear, but for TiO₂ (anatase) and SiO₂ it is S-shaped, with the greatest increase in conductivity observed between 58 and 81% RH (see Fig. 6). Furthermore, at higher temperatures, the conductivities of TiO₂ and SiO₂ increase significantly, whereas for Al₂O₃, conductivity does not increase nearly as much. The variation of the conductivity was linear with temperature for SiO₂, and exponential for TiO₂ and Al₂O₃. At 81% RH, 3.9x10⁻³ S/cm and 4.0x10⁻³ S/cm were measured for TiO₂ and SiO₂, respectively. It must be taken into account that the SiO₂ xerogel was previously treated with HNO₃ acid and, as demonstrated by Colomer and Anderson [38], after treatment with HNO₃ acid, SiO₂ xerogels showed a better proton conductivity under the same temperature and relative humidity. For instance, when silica xerogels are treated with HNO₃ acid at pH 1.5, their proton conductivity increased from 2.84x10⁻³ to 4.0x10⁻³ S/cm

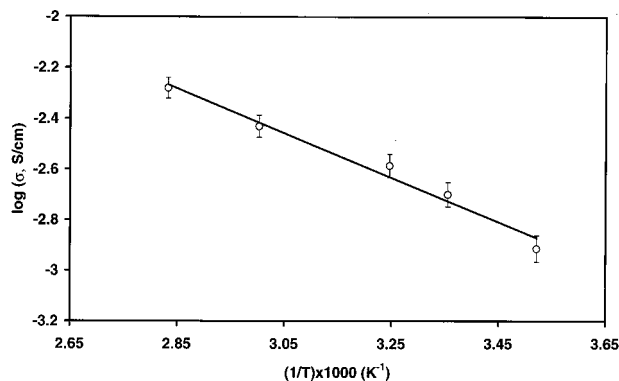


Figure 6. Dependence of conductivity with temperature for silica xerogels with a porosity value of 48.0% and an average pore size of 3.5 and 6 nm (data obtained at 81% RH) according to Colomer and Anderson [38].

at 81% RH and 80°C, indicating that the surface site density has a significant effect on proton conductivity.

Colomer and Jurado [39] found higher values of proton conductivity, 7.08x10⁻³ S/cm at 80°C and 81% R.H., for untreated SiO₂ xerogels with a higher porosity (52.0%) and slightly wider average pore size distribution (average pore size 2 nm < d_{pore} size < 6.8 nm) (see figure 7).

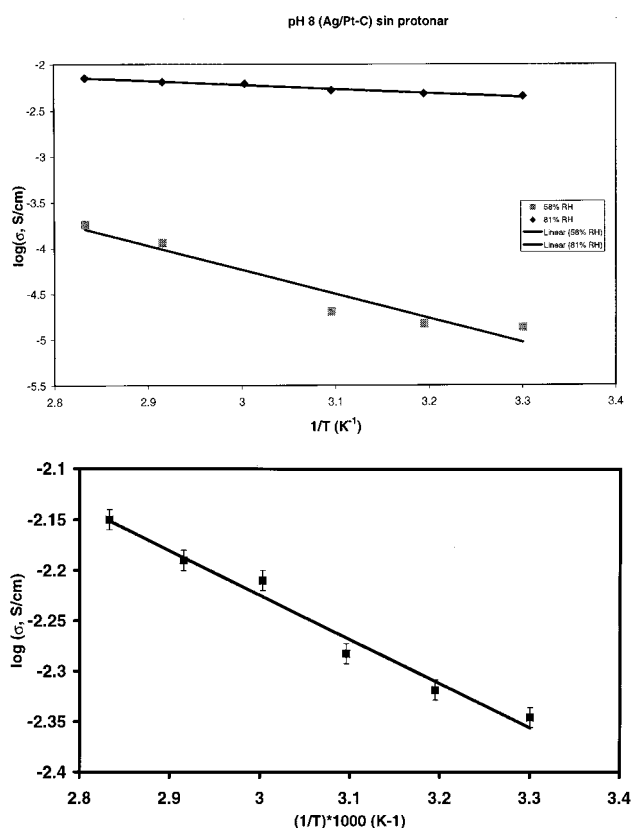


Figure 7. Logarithm of the proton conductivity (81% RH) as a function of the reciprocal of the temperature (1/T) for a SiO₂ xerogel with a porosity value of 52.0% and an average pore size of 2 nm < d_{pore} size < 6.8 nm, according to Colomer and Jurado [39].

Vichi et al. [22] prepared mesoporous xerogels of TiO₂ with an average pore size of 7.7 nm and a porosity value of 47.0% by the controlled drying of precursor sols. The TiO₂ sols were synthesized by hydrolysis of the titanium isopropoxide and dialyzed following a procedure described elsewhere [40]. Vichi et al. [41] suggested that the process of water adsorption in this material takes place in two stages. At lower relative humidity, the water forms a layer of clusters along the wall (interfacial layer) of a matrix of interconnected pores. At higher RH, however other water molecules start filling the remaining pore space through capillary condensation. These authors also reported [41] the proton conductivity values obtained by impedance spectroscopy at room temperature and at different RH. The conductivity values increased with increasing water content. The proton conductivity values did not totally correlate with the water content of a sample. This indicates that differences in both proton concentrations and proton mobility in the pore wall exist. The conductivity of the TiO₂ porous xerogels, especially those treated at pH 1.5 was very close to that of Nafion (1.00x10⁻² S/cm at 25°C and 81% RH).

Although the values of proton conductivity for treated TiO₂ or untreated SiO₂ xerogels are very close to that of Nafion, thin films of this type of material are required for their use as electrolyte in PEMFCs. It is necessary to show that films with the same texture and proton conductivity as that of xerogels can be obtained.

SOLID ACIDS

Solid, inorganic, acid compounds (or simply, solid acids), such as CsHSO₄ and Rb₃H(SeO₄)₂, have been widely studied because of their high proton conductivities and phase-transition behaviour. For fuel-cell applications, they offer the advantages of anhydrous proton transport and high-temperature stability (up to 250°C). Until now, however, solid acids have not been considered viable fuel-cell electrolyte alternatives owing to their solubility in water and extreme ductility at raised temperatures (above approximately 125°C). Haile et al. [42] showed that a cell made of a CsHSO₄ electrolyte membrane (about 1.5 mm thick) operating at 150–160°C in a H₂/O₂ configuration exhibits promising electrochemical performances: open circuit voltages of 1.11 V and current densities of 44 mA/cm² at short circuit. Moreover, the solid-acid properties were not affected by exposure to humid atmospheres. Although these initial results were promising for possible electrolyte applications, the use of solid acids in fuel cells will require the development of fabrication techniques to reduce electrolyte thickness, and an assessment of possible sulphur reduction following prolonged exposure to hydrogen [42].

CONCLUSIONS

The growing importance of cleaner energy requires the proton as a charge carrier and increases the need for materials with higher proton conductivity for

fuel cells. In particular, polymer-based proton conductors are quickly approaching the market for PEMFCs. However, not only polymers are being studied. Environmentally friendly materials, such as nanopore ceramic membranes and glasses, are being developed as possible candidates to replace Nafion.

Sol-gel processes play a key role in the synthesis of ceramic membranes, and glasses, which need both controlled pore size and porosity.

Although a great effort is being carried out by many researchers on glasses and ceramic membranes, some problems are still unsolved. The ability to form defect-free, highly conductive, micro- and mesoporous films on C/Pt electrodes through coating processes is required for using nanopore ceramic membranes and glasses as electrolytes in PEMFCs.

The chemical durability of proton conductor glasses is a crucial problem in this field, since the glasses must tolerate high water-vapour partial pressures under operation conditions.

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