

COMPOSITE MEMBRANES FOR MEDIUM-TEMPERATURE PEM FUEL CELLS

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■ **Abstract** The main obstacles to greater commercialization of polymer electrolyte fuel cells are mostly related to the low-proton conductivity at low-relative humidity of the known ionomeric membranes, to their high methanol permeability and poor mechanical properties above $\sim 130^{\circ}\text{C}$. A possible solution for these problems has been found in the development of composite membranes, where particles of suitable fillers are dispersed in the ionomer matrix. The preparation methods for obtaining composite membranes are described, and recent work dealing with composite ionomeric membranes containing silica, heteropolyacids, layered metal phosphates, and phosphonates is reviewed. Finally, new strategies for the preparation of nano-composite membranes and for the filling of porous polymeric membranes with highly conductive zirconium phosphonates are described. The expected influence of size and orientation of these particles on membrane properties, such as conductivity and permeability to methanol, is also discussed.

INTRODUCTION

Numerous types of the so-called PEM FCs (polymer electrolyte membrane fuel cells) are presently under investigation. Unfortunately, although several years of intense research have already been dedicated to their development for use in electric cars, the present state-of-the-art is still unable to produce economical PEM FCs, as clearly demonstrated by the fact that only prototypes of FC cars and buses are presently in circulation. In recent years, the necessity of a reduction of the pollution, especially in large cities, has reinforced the interest in PEM FCs, and a considerable effort to produce commercial FC vehicles is in progress.

The main obstacles to a greater commercialization seem to be related to the high cost of the known proton-conducting membranes (1), to their low-proton conductivity at low relative humidity, to the high methanol crossover, and to their poor mechanical properties above about 130°C . For example, in the case of NafionTM, which is the most advanced proton-conducting membrane, the drastic decrease of the proton conductivity at low relative humidity (2) limits the operation temperature

to about 80°C for fuel cells using these membranes. It is now becoming clear that the generalized use of pure Nafion membranes is not feasible, and new types of proton-conducting membranes, which are more economical and/or work in the temperature range of 90 to 160°C, have to be developed.

Four means of achieving this have been proposed: (a) development of membranes made of new ionomers exhibiting the desired characteristics; (b) development of new membranes in which suitable oxygenated acids (e.g., phosphoric or sulfuric acids) are solubilized in a polymeric matrix bearing basic groups (e.g., polybenzimidazole); (c) improvement of the characteristics of known ionomeric membranes by dispersing inside their polymeric matrix acids with low solubility (e.g., heteropolyacids) or particles of insoluble solids such as metal oxides, lamellar zirconium phosphates, or phosphonates; (d) development of membranes obtained by filling a non-proton conductive polymeric matrix with ionomers or inorganic particles of high-proton conductivity.

In this review we are essentially concerned with membranes obtained according to the latter two developments.

NANO-, MICRO-, AND MACRO-COMPOSITE MEMBRANES

All the nano- and micro-composite membranes considered here consist of an ionomer (usually containing acid or superacid $-\text{SO}_3\text{H}$ groups) in which inorganic or inorgano-organic solid particles are dispersed. The properties of these composite membranes not only depend on the nature of the ionomer and the solid used but also on the amount, homogeneous dispersion, size, and orientation of the solid particles dispersed in the polymeric matrix. In ionomers such as Nafion, where well-separated hydrophilic and hydrophobic domains are present (see below), the distribution of the dispersed particles in the different domains is also important.

In the following we use the specific terms nano-composite or micro-composite when the size of the dispersed particles is of the order of nano- or micrometers respectively, whereas the general term composite is reserved for membranes in which the size of the particles is not known. The higher the interface interaction between the polymer and dispersed particles, the greater is the filler influence on the original characteristics of the polymers. Due to the high specific surface of the nano-particles, the interface interaction with the polymer matrix can become very high and can have a great influence on the properties of the polymer itself. Thus nano-particles are expected to modify the original characteristics to greater extent than micro-particles. The nano-composite membranes are often called hybrid membranes, especially when the original characteristics of the polymeric matrix are appreciably modified.

In membranes prepared according to development (d) (see above), only particles of high-proton conductivity are used. Furthermore, in order to make the membrane proton conductive, the particles must be aggregated along continuous pathways. To make a clear distinction from micro- and nano-composite

membranes, these membranes are called macro-composite because the inorganic and organic domains are well separated. In principle, a macro-composite membrane could be prepared by introducing proton-conducting inorganic particles along continuous pathways inside an insulating polymeric structure. Suitable methods for obtaining this particular arrangement are presently not available and, in practice, an appreciable number of these pathways connecting the two external faces of the membrane can be obtained only by introducing high contents of inorganic solids. On the other hand, the mechanical characteristics of composite membranes with high filler content are very poor. Thus it is preferable to obtain these pathways by filling preformed pores with particles of high-protonic conductivity. In the following, this type of macro-composite membranes is indicated as filled porous membranes. The proton-conducting characteristics of these membranes depend on the degree of porosity, and on size and distribution (or tortuosity) of the preformed pores, as well as on the nature of the filler and the degree of pore filling. In the case of fibrous or lamellar particles, the proton conductivity also depends on their orientation inside the pores (see below).

In this review we are concerned only with composite membranes containing inorganic or inorgano-organic proton-conducting particles, and porous membranes filled with proton-conducting ionomers (e.g., porous teflon-filled with Nafion) are not discussed. It is clear that the preparation method of a composite membrane is very important, thus before examining the particular properties of the various composite membranes, we give a brief description of the present state-of-the-art methods of preparing nano-, micro- and macro-composite proton-conducting membranes.

MAIN PREPARATION METHODS

Preparation of Nano- and Micro-Composite Membranes

Nano- and micro-composite membranes can be prepared according to two main procedures: (a) dispersion of micro- or nano-sized filler particles in an ionomer solution followed by casting and (b) growth of the filler particles within a preformed membrane or in an ionomer solution.

DISPERSION OF PREFORMED PARTICLES IN AN IONOMER SOLUTION FOLLOWED BY FILM CASTING The first attempts to disperse proton-conducting inorganic particles in an ionomer solution followed by film casting were performed over 20 years ago (3–9). In procedures of this type, the solids are first ground until a fine powder is obtained and then dispersed under strong stirring in an organic solution of the polymer. The membrane is obtained by film casting and solvent elimination. The method is very simple, but it is usually difficult to avoid the formation of particle agglomerates inside the polymeric matrix, even by the use of ultrasound, and thus membranes containing non-homogeneous dispersions of micro-sized particles are usually obtained. Therefore, where possible, this simple method must

be replaced by other methods that lead to more homogeneous dispersions and, in particular, to the formation of nano-particles.

Particles exhibiting high-proton conductivity can be added even to non-conductive polymers in order to confer some proton conductivity to the composite membranes. Nevertheless, it is easy to see that in this case the conductivity is essentially related to particle-particle paths connecting the external faces of the membrane. Therefore, in the absence of suitable segregation inside the polymeric matrix that favors the formation of these paths, the conduction through particle-particle paths becomes appreciable only for high contents (>50% V/V) of added particles.

Where possible, the addition of colloidal particles is preferred to powdered solids because the particles are very small and homogeneous dispersions are usually obtained. Colloidal dispersions of hydrous oxides in aqueous solution are easily obtained by hydrolysis of metal alkoxides. Transfer of nanometer-sized silica particles from commercial aqueous silica suspensions to higher boiling point solvents such as *N*-methyl-2-pyrrolidinone (NMP) has been described (10). According to this procedure, the aqueous dispersion of the oxide is stratified over the polymer solution in the organic solvent. As water is evaporated, the oxide nano-particles transfer to the organic phase.

Most of the research on composite membranes containing layered particles has been done with layered metal(IV) acid phosphates. Figure 1 shows the typical structure of a single lamella of α -Zr(O₃P-OH)₂ and γ -ZrPO₄[O₂P(OH)₂]. The exfoliation of α -Zr(O₃P-OH)₂ · H₂O (hereafter called α -ZrP) with formation of colloidal dispersions in aqueous solution was first obtained in our laboratory over 20 years ago (11); more recently, the exfoliation of γ -ZrPO₄[O₂P(OH)₂] · 2H₂O (usually called γ -zirconium phosphate) in 1:1 water/acetone mixtures has also been performed with success (12).

Because the composite membrane is obtained by casting an ionomer solution in organic solvents, colloidal dispersions of exfoliated layered materials must be formed in the ionomer solvent or in similar solvents. Dispersions of lamellar α -ZrP particles in solvents such as dimethylformamide (DMF) or NMP have been recently obtained in our laboratory by means of intercalation-deintercalation processes. More specifically, intercalation-deintercalation of propylamine in water solution is used to exfoliate α -ZrP microcrystals into single layers and to cause subsequent partial layer re-aggregation. The resulting gelatinous precipitate is repeatedly washed with the organic solvent so that a semitransparent dispersion containing 2–4 wt% α -ZrP is obtained (13). Depending on the degree of crystallinity of the starting material and on the conditions used in the deintercalation process, it is possible to obtain dispersions of lamellar particles with thickness ranging from ~10 to 100 nm and surface area from ~0.1 to 10 μm^2 .

IN SITU FORMATION OF INORGANIC PARTICLES In situ formation of inorganic fillers in preformed membranes is usually carried out in two steps: (a) incorporation of a filler precursor in the polymeric matrix by simple impregnation (if the filler is neutral) or by ion-exchange reaction (if the filler is a cationic species) and

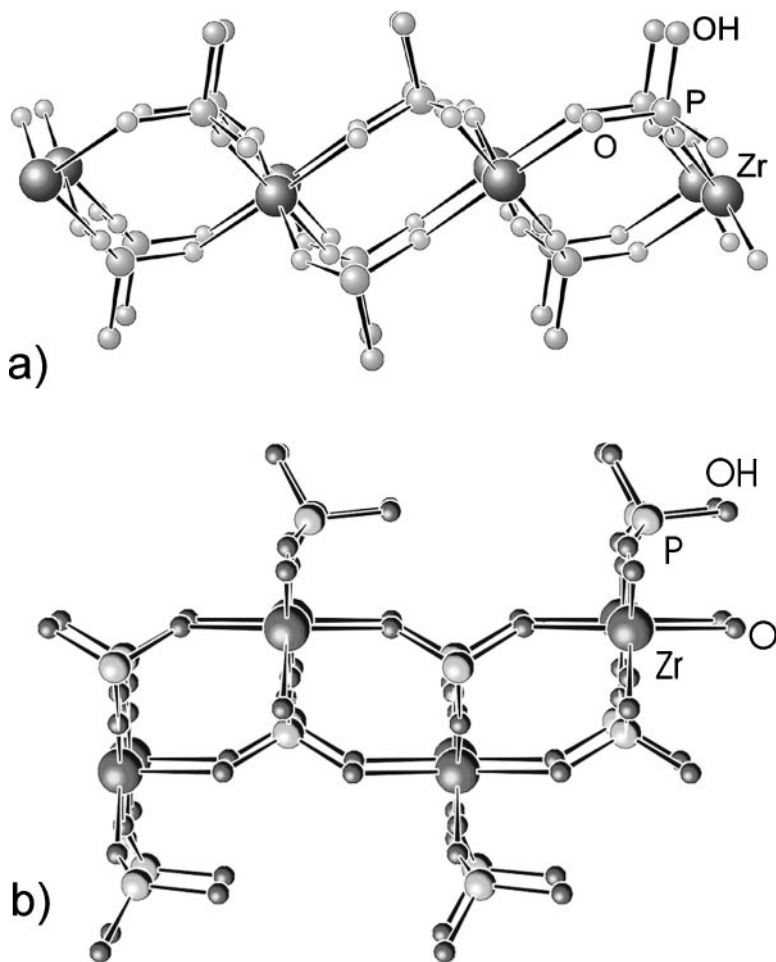


Figure 1 Single lamella structure of (a) α -ZrP and (b) γ -ZrP.

(b) subsequent treatment of the membrane with the necessary reactants to convert the precursor into the final inorganic filler (14). If this reaction is an acid-catalyzed hydrolysis, then the protogenic function of the ionomer itself can act as a catalyst, and external reactants are not necessary. A typical example is the impregnation of ionomeric membranes with tetraethoxysilane (TEOS), which is then converted, in the final filler, SiO_2 (15). From a practical point of view, in situ formation of the filler appears to be a suitable way to modify commercial membranes, which are prepared by extrusion.

A different approach, recently discovered in our laboratory, can be used for the in situ formation of layered metal(IV) phosphonates or phosphate-phosphonates (16). These compounds can be considered organic derivatives of α -ZrP and have

the general formula $M(IV)(O_3P-G)_{2-x}(O_3P-ArX)_x$, where $-G$ may be an inorganic (e.g., $-OH$) or organic (e.g., CH_2OH) or an inorgano-organic group (e.g., $-CF_2PO_3H_2$). Ar is an arylene group (e.g., phenylene); X is an acid group (e.g., $-SO_3H$, $-PO_3H_2$, or $-COOH$); x is a coefficient that can vary between 0 and 1.5. For example, for $M(IV) = Zr$, $-G = OH$, and $x = 0$, we have the compound α - $Zr(O_3P-OH)_2$. Similarly, for $-G = OH$, $-Ar = -C_6H_4$, $-X = -SO_3H$, and $x = 1$, we have the compound $Zr(O_3P-OH)(O_3P-C_6H_4-SO_3H)$. A single lamella of this compound is shown in Figure 2. Note that for the presence of the electronegative O_3P- group attached to the same ring, the $-SO_3H$ group acquires superacid properties. The value of the Hammett acid function (-5) is intermediate between those of Nafion and sulfonated polyetherketone (s-PEK). Furthermore, owing to the high hydrophilicity of $-SO_3H$ groups, the sulfophenylen derivatives exfoliate spontaneously in water. The reader interested in the chemistry of layered metal phosphonates is referred to Reference (17) and to chapters 4 and 12 of Reference (18).

In Table 1, the conductivity of some zirconium phosphonates is reported and compared with that of α - and γ -zirconium phosphates of various crystallinity. Note that the conductivity of the sulfophenylen derivatives is much higher than that of the best amorphous ZrP and that, for some compositions, it is comparable or even greater than that of Nafion 117. The in situ formation of these insoluble layered compounds is based on the experimental observation that their soluble precursors can be formed in proton acceptor solvents commonly used for the solubilization of proton-conducting ionomers (e.g., DMF, NMP, alkanols, etc.). The peculiarity

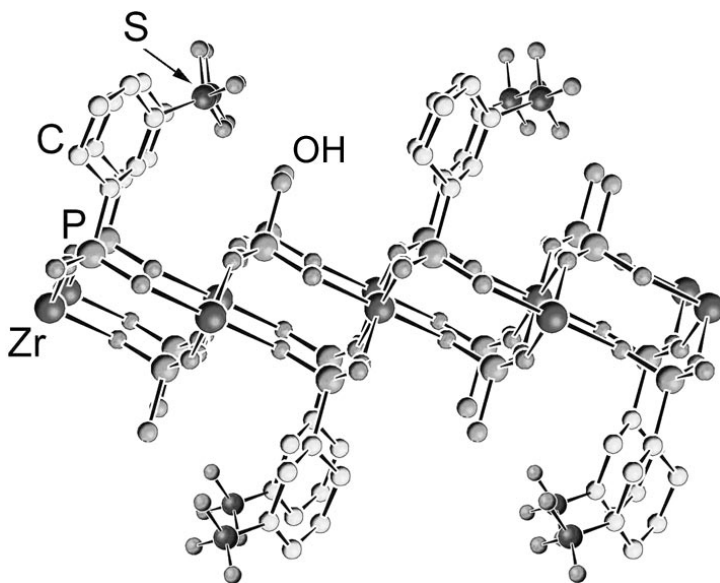


Figure 2 Single lamella structure of $Zr(O_3P-OH)(O_3P-C_6H_4SO_3H)$.

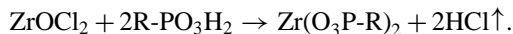
TABLE 1 Conductivity (σ) of some layered zirconium phosphates and phosphonates (100°C, 95% relative humidity)^a

	σ (S cm ⁻¹)	Reference
α -Zr(O ₃ P-OH) ₂ · H ₂ O (crystalline)	$1.8 \cdot 10^{-5}$	19
γ -ZrPO ₄ [O ₂ P(OH) ₂] ₂ · 2H ₂ O (crystal.)	$2 \cdot 10^{-4}$	20
α -Zr(O ₃ P-OH) ₂ · H ₂ O (semicrystal.)	$2-7 \cdot 10^{-4}$	4
Zr(O ₃ P-OH) ₂ · nH ₂ O (amorphous)	$1-5 \cdot 10^{-3}$	a
Zr(O ₃ P-OH) _{1.5} (O ₃ P-C ₆ H ₄ SO ₃ H) _{0.5} (amorphous)	$0.9-1.1 \cdot 10^{-2}$	a
γ -ZrPO ₄ [O ₂ P(OH) ₂] _{0.54} [O ₂ P(OH)C ₆ H ₄ SO ₃ H] _{0.46} · nH ₂ O (crystal.)	$5 \cdot 10^{-2}$	20
Zr(O ₃ P-OH)(O ₃ P-C ₆ H ₄ SO ₃ H) · nH ₂ O (semicrystal.)	$0.8-1.1 \cdot 10^{-1}$	a

^aG. Alberti & M. Casciola, unpublished results.

of these soluble precursors is that they can be easily transformed into the final insoluble zirconium phosphonates just by drying at 110–130°C.

The exact nature of these soluble precursors is presently under investigation. It is well known that the reaction between a zirconyl salt and phosphonic acids in aqueous solution leads to the quick formation of insoluble layered zirconium phosphonates:



In an organic, proton-acceptor solvent, the precipitation does not occur. Probably, the interaction of the solvent with the phosphonic acid lowers the acid activity. Thus the transformation rate of the zirconyl into the zirconium salt could be very slow. As matter of fact, these solutions, especially at temperatures lower than 20°C, remain stable for many days. By increasing the temperature, the transformation rate increases appreciably. At 80°C, the formation of dense gels is already observed in less than 1 h. The nature of these gels is unknown. It is likely that they are formed by small clusters of layered zirconium phosphonates, with the solvent intercalated in their interlayer region because insoluble zirconium phosphonates are obtained by drying. In any case, although additional studies have to be carried out to better clarify the nature of these solutions, they are of great practical importance for the preparation both of nano- and macro-composite membranes.

A typical preparation of a Nafion nano-composite membrane containing 10.4 wt% of anhydrous Zr(O₃P-OH)(O₃P-C₆H₄SO₃H) is given here as an example: A precursor solution of the above compound is prepared by solubilizing 0.1 mol of anhydrous zirconyl propionate (Magnesium Elektron Limited; England) in 200 g of propanol. Separately, 0.1 mol of anhydrous metasulfophenylene phosphonic acid and 0.1 mol of anhydrous phosphoric acid are also solubilized in 200 g of propanol. The first solution is slowly added, under vigorous stirring, to the second solution (at room temperature), thus obtaining a clear solution of the precursor

corresponding to 11.6 wt% of the anhydrous proton conductor. A weighed amount of the above precursor solution (1 g) is mixed, under stirring at room temperature, with 20 cm³ of a Nafion solution (37.5% 1-propanol, 37.5% 2-propanol, 20% water; 5% Nafion). Transparent composite membranes are obtained by casting. The solvent is eliminated by drying for about 1 h at 80–90°C and then for about 2–3 h at 120–130°C. The use of these precursor solutions for the preparation of filled porous membranes is discussed further below.

Preparation of Filled Porous Polymeric Membranes

The first attempts to produce proton-conducting membranes made of supported inorganic particles are not recent. For example, membranes of ZrP supported on glass fiber felts were prepared and characterized more than 40 years ago (21, 22). The problem of preparing filled porous membranes with good characteristics is not simple because obviously water-soluble proton-conducting particles cannot be used, and those that are insoluble in water are also insoluble in organic solvents.

DIRECT FILLING BY FILTRATION OF NANO-PARTICLES Attempts to fill the pores of polymeric membranes simply by filtration of finely dispersed precipitates of inorganic proton conductors have been performed (23). In the case of ZrP, this procedure is laborious because several filtrations of freshly formed precipitates must be carried out. In our experience, preformed ZrP-exfoliated lamellae (even of dimensions as small as 0.5–1 μm²) have a strong tendency to obstruct pores narrower than 5 μm. It is likely that faster diffusion of the solvent in the pores favors the re-aggregation of the lamellar particles on the membrane external surfaces.

FORMATION OF M(IV) OXIDES AND PHOSPHATES WITHIN THE POROUS STRUCTURE

The in situ formation of metal hydrous oxides can be performed by using organic precursors such as metal alkoxides. For example, the void portion of a porous substantially inert polymer such as porous teflon can be first filled with a solution of a metal(IV) alkoxide. By exposing this membrane to wet air, insoluble M(IV) hydrous oxide is formed directly inside the membrane pores. The modest protonic conductivity of these membranes can be enhanced by treatment with phosphoric acid, which converts the M(IV) hydrous oxide into the corresponding acid phosphate. This filling procedure requires many impregnations with the filler precursor and an accurate washing of the membrane to eliminate the excess of phosphoric acid. Furthermore, based on our experience, the full conversion of the metal hydrous oxide is often not reached.

Alternatively, the porous membrane can be placed between a solution of a zirconyl chloride and phosphoric acid to allow the direct precipitation of amorphous ZrP within the membrane pores (9).

FORMATION OF M(IV) ACID PHOSPHONATES WITHIN THE POROUS STRUCTURE

As seen above, the filling of porous membranes with insoluble inorganic proton

conductors presents many difficulties. Taking advantage of the organic solutions of zirconium phosphonate precursors (already described for the preparation of nano-composite membranes), a new filling procedure has recently been developed in our laboratory. From a practical standpoint, these solutions behave as solutions of insoluble compounds because insoluble zirconium phosphonates are obtained when the solvent is eliminated. Thus they can be used for the filling of both ceramic and polymeric porous membranes with inorgano-organic compounds of high-proton conductivity.

As an example, a typical procedure for the filling of a porous polytetrafluoroethylene (PTFE) with the proton conductor $\text{Zr}(\text{O}_3\text{P}-\text{OH})(\text{O}_3\text{P}-\text{C}_6\text{H}_4\text{SO}_3\text{H})$ is given: A precursor solution of 0.1 mol of the compound in 192 g of propanol (i.e., 18 wt%) is first prepared (see the above procedure). A millipore PTFE membrane (fluoropore membrane filter, pore diameter 0.5 μm ; porosity 85%) is completely covered with this solution at room temperature for about 2 h (16). The excess of liquid is removed and the solvent is eliminated by drying for 1 h at 80°C and then for ~ 3 h at 130°C. The procedure is repeated four to five times in order to fill ~ 70 –80% of the pore volume with the anhydrous compound. Complete filling is finally obtained when the anhydrous compound is hydrated (the compound takes up about 14 H_2O per $-\text{SO}_3\text{H}$ group when conditioned at 100% relative humidity).

PROPERTIES OF PROTON-CONDUCTING COMPOSITE MEMBRANES

Metal Oxide-Filled Membranes

PERFLUORINATED POLYMERS The first nano-composite Nafion-SiO₂ membranes were obtained by growing the silica particles inside a preformed membrane (15, 24–29). According to the procedure described above, TEOS is incorporated into Nafion membranes, previously swollen with alcohol and water, and then hydrolyzed via a sol-gel reaction confined within the polar clusters and catalyzed by the superacid sulfonic groups of the clusters. The in situ grown silica is represented by the formula $\text{SiO}_{2(1-x/4)}(\text{OH})_x$, with x significantly higher than zero. Characterization of these nano-composites by FT-IR spectroscopy (15), dielectric relaxation (24), thermal analysis (25), and small angle X-ray scattering (SAXS) (26) suggests that the nano-phase-separated morphology of Nafion acts as a template for the growth of the incorporated silica phase. More specifically, the SAXS peak characteristic of quasi-ordered clusters in unfilled Nafion persists in the composites filled with silica. In situ hydrolysis of metal alkoxides was also used to prepare a number of nano-composite Nafion membranes containing zirconium oxide (30), mixed silicon-titanium oxide, and mixed silicon-aluminium oxide (31). In spite of the broad investigative work on the structural features of these composites, conductivity data are presently available only for Nafion 117 membranes with non-uniform SiO₂ distribution (29). The conductivity of membranes containing an overall Si/SO₃H concentration ratio of 5 ($\sigma = 9.9 \cdot 10^{-2} \text{ S cm}^{-1}$ at 80°C and 100% relative humidity)

was found to be slightly higher than that of the unmodified membrane under the same conditions ($\sigma = 7.4 \cdot 10^{-2} \text{ S cm}^{-1}$).

Nafion-SiO₂ composite membranes were also obtained by hydrolysis/polycondensation of alkoxy silanes in water-propanol Nafion solutions (32, 33). Because the growth of the inorganic polymer is not limited to already existent ionic clusters, this approach offers the possibility of obtaining diverse morphologies depending on the amounts of the incorporated inorganic component. Transparent but brittle films, containing up to 54 wt% silica, were obtained by using TEOS as a precursor of the inorganic polymer. The film flexibility was increased by replacing 1,1,3,3-tetramethyl-1,3-diethoxydisiloxane (TMDES) for TEOS. However, for substitution higher than 10%, phase separation was observed by electron microscopy. The conductivity of these films was determined by impedance measurements in the range of 25–100°C in an argon atmosphere. The highest conductivity ($\sigma \approx 2 \cdot 10^{-3} \text{ S cm}^{-1}$ at 100°C) was found for the film prepared starting from a Nafion/TEOS/TMDES mixture of composition 50/40/10 wt%, respectively. Unfortunately, a direct comparison with the conductivity of Nafion under the same experimental conditions is missing.

On the basis of the same synthetic approach, a significant enhancement of the conductivity of Nafion 117 and recast Nafion was achieved with Nafion-bifunctional silica composite membranes, where sol-gel-derived silica particles have both -SiOH and -SO₃H functional groups (34). These membranes were prepared by casting Nafion-ethanol solutions mixed with sulfonated phenethylsilica sol. Due to the presence of sulfonated silica, ion exchange capacity of these membranes increases linearly with silica-loading from $0.9 \cdot 10^{-3} \text{ mol -SO}_3\text{H g}^{-1}$ for bare recast Nafion up to about $2 \cdot 10^{-3} \text{ mol -SO}_3\text{H g}^{-1}$ for 7.5 wt% silica. Concomitantly, the water content per gram of dry membrane grows from 0.26 to 0.4 g at room temperature, and from 0.36 to 0.7 g at 80°C. However, the degree of hydration, expressed as number of water molecules per sulfonic group, is fairly constant and nearly coincident with that of Nafion 117. Therefore, solvation of the products of ionization of the highly acidic sulfonic function (H⁺, -SO₃⁻), rather than water interaction with the hydrophilic -SiOH groups, appears to be the driving force for membrane hydration. At 80°C and 100% relative humidity, the conductivity of composite membranes loaded with 2.5–5 wt% silica ($\sigma = 0.11$ and 0.23 S cm^{-1} , respectively) is 2.7–5.8 times higher than that of Nafion 117 under the same conditions.

Nano-composite Nafion membranes containing 3 wt% SiO₂ or TiO₂ were also prepared by bulk mixing of a polymer solution with oxide nano-crystallites (5–7 nm size) followed by casting. These membranes, 50 μm thick, were then loaded with highly dispersed platinum (0.07 mg/cm²) by ion-exchange of Pt(NH₃)₄²⁺ and subsequent Pt reduction with hydrazine. When used as proton electrolytes in fuel cells, these membranes effectively suppressed H₂ and O₂ crossover and allowed efficient operation at 80°C even without gas humidification (35, 36). This is possible because the Pt particles catalyze the combination of crossover hydrogen and oxygen to generate water, which in turn is retained by the membrane. Metal

oxide-loaded Nafion appears to be more hydrophilic than unmodified Nafion: the water content of Pt-loaded Nafion is reported to increase from 18 to 41 wt% in the presence of 3 wt% silica. This is usually accounted for by water absorption on the particles of the hygroscopic oxide. However, a simple calculation shows that the 23 wt% excess of water found for the silica loaded membrane corresponds to a molar ratio $\text{H}_2\text{O}/\text{SiO}_2 \sim 27$. Taking into account that water is adsorbed only on the surface of silica nano-particles, the hydration number of surface silanol groups ($\text{H}_2\text{O}/\text{-SiOH}$) must be much greater than 27 mol/mol. On the other hand, the hydration number for $\text{-SO}_3\text{H}$ groups of a Nafion membrane containing 18 wt% water is ~ 11 mol/mol. The fact that a silanol group is expected to be much more hydrated than a superacidic sulfonic function seems to be unrealistic. Therefore, the increased water content of metal oxide-loaded Nafion can hardly be ascribed to the hygroscopic character of the oxide and is probably associated with structural changes of the polymeric matrix induced by the presence of the inorganic nano-particles. From the point of view of practical applications, it must be pointed out that Pt-loaded Nafion membranes are very expensive and that, in the absence of platinum, silica-loaded membranes show a poor fuel cell performance when fed with anhydrous gases (35).

Thermal treatment of Nafion 3-wt% SiO_2 nano-composite membranes by hot pressing up to 160°C was shown to increase the polymer crystalline fraction (37, 38). Direct methanol fuel cells based on this type of membrane and fed with 2 M methanol were characterized by low methanol crossover and were able to work up to 145°C with open circuit voltages of 0.82–0.95 V and power density peaks of 150–240 mW/cm^2 in air and oxygen, respectively.

NON-FLUORINATED POLYMERS High-surface amorphous silica, precipitated from a solution of a tetrapropylammonium oligosilicate, was used as a filler of sulfonated poly(ether ether ketone) (s-PEEK) having 1.6 mequivalent/g ion-exchange capacity (39). Micro-composite membranes containing up to 20 wt% silica were prepared by bulk mixing of the finely ground powder with the polymer solution. The membrane containing 10 wt% silica exhibited the best electrical and mechanical characteristics. Its conductivity at 100°C raises from $8 \cdot 10^{-3}$ to $9 \cdot 10^{-2} \text{ S cm}^{-1}$ for relative humidity increasing in the range of 75–100%, and is up to two times higher than that of the unmodified polymer. At 100% relative humidity, the conductivity is nearly independent of temperature between 80 and 130°C , but it decreases down to $3 \cdot 10^{-2} \text{ S cm}^{-1}$ at 160°C .

A silica network derived from TEOS was grown in a solution of s-PEEK and, at the same time, the network surface was functionalized by reaction with aminophenyltrimethoxysilane (APTMS) (10, 40). Protonation of the surface aminophenyl groups by the polymer $\text{-SO}_3\text{H}$ groups prevents auto-aggregation of the silica particles and allows the formation of well-dispersed nano-sized silica. The interaction between -NH_3^+ and -SO_3^- groups provides some ionic crosslinking between polymer and filler. Accordingly, while non-functionalized silica causes a worsening of the mechanical properties of the composites, membranes containing

APTMO-functionalized silica show the same and, in some cases, even higher mechanical modulus than unmodified s-PEEK. Flexible and transparent nano-composite membranes containing up to 50 wt% silica were obtained by using DMSO as a solvent. However, with solvents of lower dielectric constant, such as DMF or NMP, the ionic crosslinking is insufficient to ensure complete dispersion of the inorganic phase above 30 wt% loading. In spite of the high loading of a low-proton-conducting inorganic phase, the conductivity of membranes containing 50 wt% silica is maintained above $10^{-2} \text{ S cm}^{-1}$ at 25°C .

According to a similar synthetic approach, nano-composite membranes loaded with SiO_2 , TiO_2 , and ZrO_2 were prepared by hydrolysis of silanes and metal alkoxides in solutions of s-PEEK and s-PEK (41). While homogeneous dispersions of TiO_2 and ZrO_2 particles were obtained starting from $\text{Ti}(\text{OEt})_4$ and $\text{Zr}(\text{OPr})_4$, the hydrolysis of $\text{Si}(\text{OEt})_4$ led to the formation of larger particles and cavities in the polymeric matrix. However, smaller and better-dispersed silica particles ($\sim 100 \text{ nm}$ size) were formed by using either silanes covalently bonded to the polymer chain or organically modified silanes bearing imidazole groups. A loading of 14–33 wt% metal oxide resulted in a decrease of the membrane permeability to water and methanol by a factor of 30–60 but also resulted in a reduced proton conductivity at 25°C . A good balance of low permeability and high conductivity ($3.5\text{--}4.5 \cdot 10^{-3} \text{ S cm}^{-1}$ against $5 \cdot 10^{-3} \text{ S cm}^{-1}$ for the unmodified polymer) was achieved by incorporation of a mixture of 10–15 wt% ZrO_2 and 20–14 wt% amorphous ZrP in s-PEEK.

Heteropolyacid-Filled Membranes

Heteropolyacids, in addition to being electrocatalytically active (42, 43), possess strong acidity and high-proton conductivity in their hydrated form (44). Most of them exhibit the Keggin structure, and their molecules (about 1 nm in diameter) can be regarded as nano-particles. Owing to these characteristics, heteropolyacids are suitable membrane fillers for increasing the number of protonic carriers and thus improving the hydrophilic character of the membranes.

PERFLUORINATED POLYMERS Composite Nafion membranes containing heteropolyacids were obtained by simple impregnation of preformed membranes with a heteropolyacid solution (45) and by mixing a Nafion solution with an appropriate amount of a heteropolyacid followed by casting (46, 47). Nafion recast membranes loaded with silicotungstic acid (STA), phosphotungstic acid (PTA), and phosphomolybdic acid (PMA) were systematically investigated by ionic conductivity, water uptake, tensile strength, and thermal behavior determinations.

In comparison with Nafion 117, all these membranes exhibited higher proton conductivity and greater water uptake, but decreased tensile strength. Water uptake, determined by dipping dried membranes in boiling water, increases from 27% for Nafion 117 to a maximum of 95% for the PMA-based membrane. At 80°C , the heteropolyacid-loaded membranes show a better fuel cell performance than

unmodified Nafion 117. The current density at 0.600 V increases from 640 mA/cm² for Nafion 117 up to a maximum of 940 mA/cm² for MPA-Nafion 117. Composite PTA-Nafion 117 membranes, prepared by impregnation with PTA solutions in acetic acid or in molten tetra-*n*-butylammonium chloride, were tested in H₂/O₂ fuel cells working at 1 atm up to 110°C (45). In comparison with unmodified Nafion 117, these membranes showed a strong performance enhancement that increased with increasing temperature.

NON-FLUORINATED POLYMERS A series of nano-composite membranes made of s-PEEK and 60 wt% TPA or MPA were prepared by mixing the heteropolyacid with a polymer solution in dimethylacetamide (48). In comparison with the pure sulfonated polymers, the composite membranes are characterized by a higher glass transition temperature, probably because of the intermolecular interaction between the sulfonic groups and the heteropolyacids, and by much greater hydration at room temperature (up to five times for TPA-loaded s-PEEK with 80% sulfonation degree). Conductivity determinations were carried out in the range of 20–150°C by using an open cell. The concomitant water loss occurring over the time scale of the experiment was estimated to be about 65% at 140°C. Therefore, the results of these measurements should be regarded as an evaluation of a lower limit of the membrane conductivity at a given temperature. The composite membranes are generally more conductive than the pure polymer, but the conductivity enhancement decreases with increasing the degree of sulfonation. In all cases, the conductivity dependence on temperature shows a maximum around 120°C. In the investigated temperature range, the highest conductivities were found for the TPA-based membranes ($\sigma_{120^\circ\text{C}}$ from $2 \cdot 10^{-2}$ to 0.1 S cm^{-1} with increasing degree of sulfonation from 70 to 80%).

A remarkable family of inorgano-organic polymers was developed by reacting polyethers such as PEO, PPO, PTMO with alkoxysilanes (49, 50). The synthetic procedure consists of two main steps: (a) end-capping of the organic polymer with alkoxysilanes through isocyanato coupling and (b) subsequent hydrolysis-condensation of these precursors. The resulting glassy materials consist of nano-sized silica domains interconnected by polymer chains. In the presence of water vapor, membranes made of these hybrids become proton conducting when doped with PTA, which probably is entrapped within the silica domains. Accordingly, no PTA leak out from the hybrid membrane is observed even for doping levels as high as 100 wt% with respect to the hybrid polymer. For similar molecular weights of the organic polymer, PTMO-based membranes show the highest thermal stability. Between 20 and 160°C, and at 100% relative humidity, the proton conductivity of PTMO membranes rises with temperature by three orders of magnitude: The highest σ values range from 10^{-5} to $10^{-4} \text{ S cm}^{-1}$ with increased PTA loading from 25 to 75 wt%.

Silica-immobilized phosphotungstic acid, PTA/SiO₂, or silicotungstic acid, STA/SiO₂ (51), were used as fillers of polybenzimidazole (PBI) (52–54) and recast Nafion (55). PBI-PTA/SiO₂ membranes, containing from 40 to 68 wt%

filler, were characterized by conductivity measurements as a function of temperature up to 150°C at fixed relative humidity and as a function of relative humidity at 100°C (52). For a PTA/SiO₂ weight ratio of 30/70, the conductivity increases with the filler content reaching a maximum for 60 wt% PTA/SiO₂. For this composition and for 100% relative humidity, σ values of $3 \cdot 10^{-3}$ and $1.4 \cdot 10^{-3}$ S cm⁻¹ were found at 100 and 150°C, respectively. Similar results were obtained for membranes containing 50 wt% STA/SiO₂ mixtures (53, 54). The highest conductivity ($\sigma = 1.2 \cdot 10^{-3}$ S cm⁻¹ at 160°C and 100% relative humidity) was observed for STA/SiO₂ weight ratio of 45/65. On the other hand, the conductivity of a membrane loaded with only 50 wt% STA was five orders of magnitude lower, thus indicating that hydrated silica provides the main pathway for proton conduction. It is interesting to observe that the conductivity of these heteropolyacid/SiO₂ membranes, although still too low for fuel cell applications, is only weakly dependent on relative humidity in the range 40–100%.

Nafion recast membranes filled with PTA/SiO₂ (30/70 weight ratio) and STA/SiO₂ (45/65 weight ratio), so that the silica content was in all cases 3 wt%, were prepared by bulk mixing of a 5% Nafion solution with the powdered filler and then thermally treated at 160°C (55). Tests in direct methanol fuel cells at 145°C showed that the PTA/SiO₂ membrane had better electrochemical characteristics at high current densities compared with membranes loaded with STA/SiO₂ or only 3 wt% SiO₂. Peaks of power density of 400 mW/cm² and 250 mW/cm² were reached by feeding the cell with oxygen and air.

Layered Phosphate-Filled Membranes

PHOSPHATOANTIMONIC ACIDS Layered phosphoantimonic acids (H_nSb_nP₂O_(3n+5) · xH₂O, with $n = 1$ and 3) exhibit a swelling behavior similar to that of smectite clays and strong acidic character (56). Because of its high protonic conductivity ($\sigma = 1.0 \cdot 10^{-2}$ S cm⁻¹ at 25°C and 100% relative humidity), the compound with $n = 3$ was selected as a filler of sulfonated polysulfone (s-PSU) membranes (57, 58). Micro-composite membranes, obtained by bulk mixing of powdered H₃Sb₃P₂O₁₄ with the polymer solution in dichloroethane-isopropanol, exhibited higher conductivity, lower water swelling, and lower gas permeability than unmodified s-PSU. The conductivity of these membranes showed a maximum for 8 wt% filler: For this loading, the conductivity of s-PSU with ion-exchange capacity of 1.1 mequivalent/g is enhanced by a factor of 10 and reaches $2 \cdot 10^{-2}$ S cm⁻¹ at 80°C and 100% relative humidity.

A fuel cell based on this membrane was able to run for 500 hours at 80°C under 4 bar H₂ and O₂, with a performance of 80% of that attained with Nafion. Surprisingly, these results refer to membranes containing an asymmetric distribution of particles about 10 μm in size. Although homogeneous filler dispersion was then obtained by using submicronic particles and diethyleneglycol-monoethylether (a more hydrophilic solvent than dichloroethane-isopropanol), no significant enhancement of membrane conductivity was achieved.

METAL(IV) PHOSPHATES Nafion 115 and recast Nafion were loaded with 23 and 36 wt% α -ZrP nano-particles (~ 10 – 12 nm) by exchange of Zr(IV) ions for protons followed by treatment of the exchanged membrane with phosphoric acid (59). At 100% relative humidity, the conductivity and the activation energy are close for the composite membranes and unmodified Nafion, thus indicating that the presence of α -ZrP does not significantly change the proton conduction mechanism in well-hydrated membranes. Accordingly, at 80°C , the ohmic resistance of fuel cells based on Nafion 115 and recast Nafion membranes was slightly lower than that found for the corresponding α -ZrP-loaded membranes when the cells were fed with H_2 and O_2 humidified at 99 and 88°C , respectively. However, at 130°C and with H_2 and O_2 humidified at 130°C , the nano-composite membranes displayed much better performance than unmodified Nafion (Figure 3). In particular, the polarization curve of a nano-composite recast membrane at 130°C and 3 atm was equivalent to that of the unmodified recast film at 80°C and 1 atm. Moreover, the composite membranes showed stable behavior during time at 130°C , whereas irreversible degradation affected Nafion under the same conditions. A direct methanol fuel cell based on a Nafion- α -ZrP nano-composite membrane exhibited good performance up to about 150°C , with maximum power densities of 380 and 260 mW/cm^2 under oxygen and air feed, respectively (60).

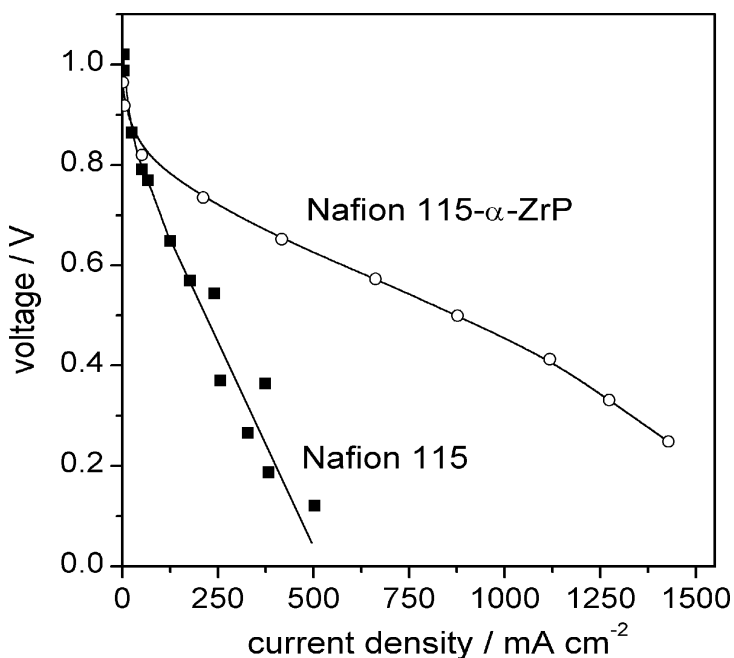


Figure 3 Polarization curves of PEM-FCs based on Nafion 115 and Nafion 115-23 wt% α -ZrP at 130°C and 3 atm with reactants humidified at 130°C [adapted from (59)].

The better fuel cell performance attained upon filling Nafion with α -ZrP nanoparticles was ascribed to enhanced water retention capability of the composite membrane. Two explanations of this phenomenon are proposed (59): replacement of unassociated pore water with hydrophilic α -ZrP nano-particles and/or capillary condensation effects due to the smaller dimensions of the free spaces in α -ZrP-filled pores.

Composite membranes based on s-PEK or s-PEEK and layered M(IV) phosphates were obtained by growing the filler within a preformed membrane and by mixing a polymer solution with a dispersion of the M(IV) phosphate. According to the second approach (13), α -ZrP particles with about 100 nm thickness and a few μm^2 surface area were dispersed in DMF and used to prepare composite s-PEK membranes with α -ZrP loading up to 20 wt%. Figure 4 (curve a) shows that, at 100°C and 100% relative humidity, the conductivity of these membranes decreases from $1 \cdot 10^{-2} \text{ S cm}^{-1}$ to $3 \cdot 10^{-4} \text{ S cm}^{-1}$ with increasing α -ZrP loading. This seems to be a consequence of the fact that large α -ZrP lamellar particles, mostly oriented with the layers parallel to the membrane surfaces, hinder proton transport perpendicular to the membrane. However, because of the particle orientation, these membranes are expected to have low-gas permeability.

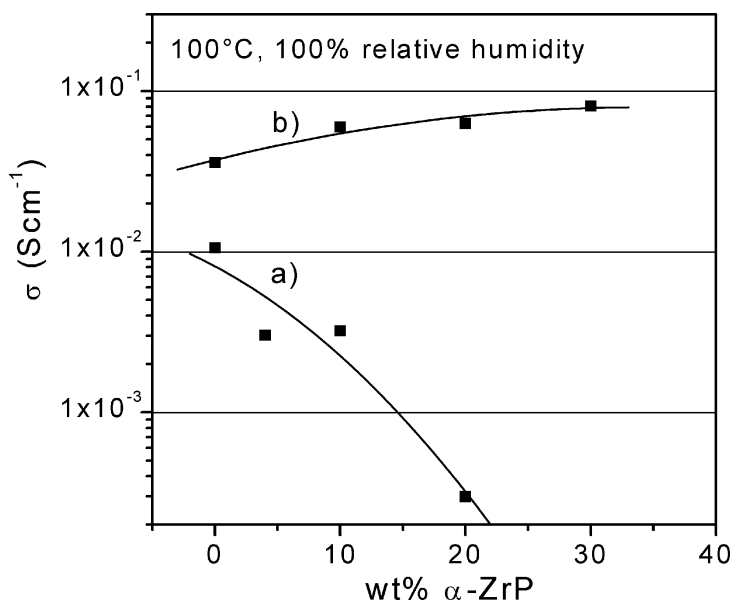


Figure 4 Conductivity as a function of filler loading for composite membranes made of (a) s-PEK (FuMA-Tech) filled with exfoliated preformed α -ZrP (G. Alberti & M. Casciola, unpublished results) and (b) s-PEEK filled with α -ZrP by in situ growth [adapted from (39)].

α -ZrP and Sn phosphate (SnP) nano-particles were grown within preformed s-PEEK membranes (39, 61, 62). The X-ray powder diffraction patterns of these membranes show few and broad reflections characteristic of α -layered ZrP and SnP. The particle dimensions estimated from the 002 reflection agree with those resulting from transmission electron microscopy (TEM) (15–30 nm for α -ZrP and 5–10 nm for α -SnP). At 100°C and 100% relative humidity, the conductivity of α -ZrP based s-PEEK membranes increases with α -ZrP loading from $4 \cdot 10^{-2} \text{ S cm}^{-1}$ (unmodified s-PEEK treated under the same conditions used for the preparation of the composite membrane) to $8 \cdot 10^{-2} \text{ S cm}^{-1}$ for 30 wt% α -ZrP (Figure 4, *curve b*). These conductivity values are nearly coincident with those obtained for the same polymer filled with 10% high surface silica; once again, the conductivity enhancement observed in the presence of α -ZrP is likely due to some modification of the polymer microstructure induced by the filler nano-particles rather than to their intrinsic conductivity. The polarization characteristics of a hydrogen fuel cell based on nano-composite s-PEEK-ZrP (25 wt%) membranes showed an improved performance as temperature was increased from 80 to 100°C.

Metal(IV) phosphates were also inserted in porous teflon membranes (see above). Conductivity data for these membranes are not reported but it is claimed, unfortunately without any experimental evidence, that they could be employed in PEM FCs (23). On the basis of our knowledge on the proton conductivity of α -ZrP of different crystallinity at various temperatures and different relative humidity, we think that this eventuality is unrealistic. Even in the fortunate case in which the conductivity of the filled membranes were near to that of amorphous ZrP, filled membranes with conductivity lower than $5 \cdot 10^{-3} \text{ S cm}^{-1}$ have to be expected (see Table 1).

Layered Metal Phosphonate-Filled Membranes

NANO- AND MICRO-COMPOSITE MEMBRANES Due to the insolubility of these layered compounds, the first composite membranes were prepared by bulk mixing of the finely ground filler with the ionomer solution (see above). Micro-composite membranes of Nafion 1100 containing up to 30 wt% of titanium phosphate sulfophenylphosphonate of composition $\text{Ti}(\text{O}_3\text{P-OH})_{1.00}(\text{O}_3\text{P-C}_6\text{H}_4\text{SO}_3\text{H})_{0.85}(\text{OH})_{0.30} \cdot n\text{H}_2\text{O}$ have been investigated (63). Their conductivity, at 100°C and 80% relative humidity, is similar to that of an unmodified Nafion recast membrane for filler loading up to 20%, but it drops by an order of magnitude when the loading is increased to 30%. Higher temperatures and the effect of filler on the mechanical properties and on the methanol crossover have not been yet investigated.

Micro-composite s-PEEK membranes containing 40 wt% amorphous zirconium phosphate sulfophenylphosphonate $(\text{Zr}(\text{O}_3\text{P-OH})_{2-x}(\text{O}_3\text{P-C}_6\text{H}_4\text{SO}_3\text{H})_x \cdot n\text{H}_2\text{O})$, with $x = 1, 1.5$ as filler have been also prepared. The conductivity of these membranes lies between those of the two components and reaches a maximum value of 0.04 S cm^{-1} at 150°C and 100% relative humidity (39).

More recently, nano-composite membranes have been prepared by using organic solutions of zirconium phosphonate precursors. Preliminary results obtained

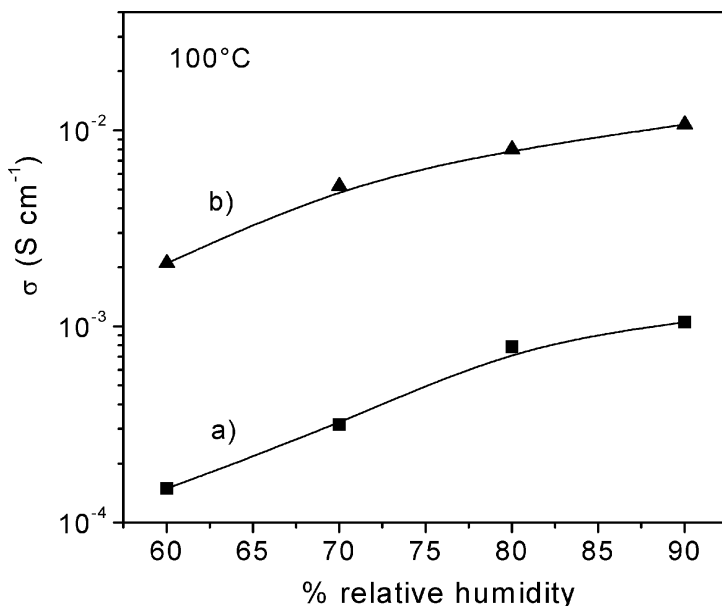


Figure 5 Conductivity as a function of relative humidity for (a) high-molecular weight s-PEK membrane (FuMA-Tech; thickness 50 μm) and (b) the same membrane filled with 35 wt% of $\text{Zr}(\text{O}_3\text{P-OH})(\text{O}_3\text{P-C}_6\text{H}_4\text{SO}_3\text{H}) \cdot n\text{H}_2\text{O}$ (G. Alberti & M. Casciola, unpublished results).

in our laboratory showed that the conductivity of s-PEK membranes of high-molecular weight (FuMA-Tech) is enhanced to a great extent in the presence of nano-particles of zirconium phosphate sulfophenylphosphonates (Figure 5). Taking into account that much lower enhancement was instead obtained with α -ZrP nano-particles, these results seem to confirm the importance of the high-proton conductivity and acid strength of the filler. Thus superacid zirconium phosphonates deserve further attention as fillers of nano-composite membranes. A systematic investigation is now in progress in our laboratory.

FILLED POROUS POLYMERIC MEMBRANES Zirconium phosphate sulfophenylphosphonates of comparable or higher conductivity than Nafion are presently available (Table 1). The use of these proton conductors in fuel cells is attractive but is seriously limited by the fact that flexible and mechanically resistant membranes can hardly be prepared with pure inorganic or inorgano-organic proton conductors. Overcoming this limitation is really of great technological importance because a large variety of these proton conductors with modulable properties can be easily prepared.

The recent discovery that precursors solutions of these insoluble compounds can be obtained in organic proton acceptor solvents has opened the way to the

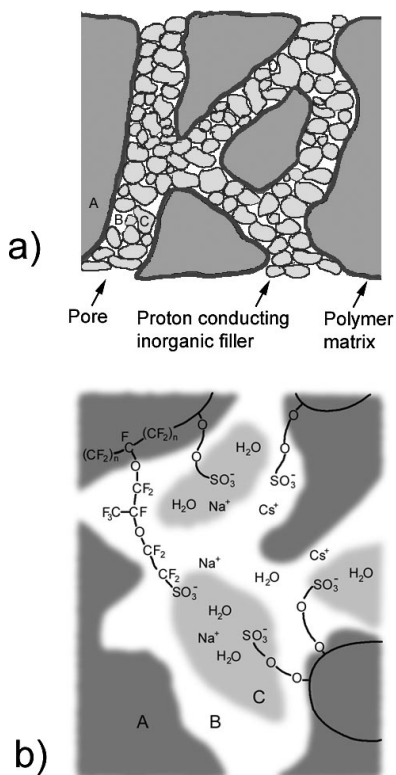


Figure 6 (a) A schematic view of a porous polymeric membrane filled with proton-conducting inorganic or inorgano-organic particles. (b) The analogy with the three-region model for Nafion (64) is shown.

preparation of porous polymeric membranes filled with these protonic conductors. The preparation method of these membranes has already been discussed (see above). A porous polymeric membrane filled with inorganic particles is schematically shown in Figure 6. In the same figure, the three-region model for Nafion (64) is also reported. The analogy between Nafion and filled polymeric membranes can be pointed out. Both membranes have a hydrophobic region (A) responsible for the mechanical properties of the membrane, a hydrophilic region (C), where superacid protogenic $-\text{SO}_3\text{H}$ groups are located, and a hydrophilic interfacial zone (B).

Figure 7 shows some results obtained in our laboratory with a porous teflon membrane filled with $\text{Zr}(\text{O}_3\text{P-OH})(\text{O}_3\text{P-C}_6\text{H}_4\text{SO}_3\text{H}) \cdot n\text{H}_2\text{O}$. The results obtained with a Nafion 117 membrane are also reported for comparison. It was found, surprisingly, that the conductivity of the filled porous membranes is about the same as that exhibited by pure pellets of $\text{Zr}(\text{O}_3\text{P-OH})(\text{O}_3\text{P-C}_6\text{H}_4\text{SO}_3\text{H}) \cdot n\text{H}_2\text{O}$. This fact seems to indicate that the decrease of the conductivity owing to the pore-connecting tortuous paths is compensated by an increased conductivity of the zirconium phosphonate formed inside the pores. This pore effect on the conductivity could be related to a preferred parallel orientation to the pore surface of the formed lamellar

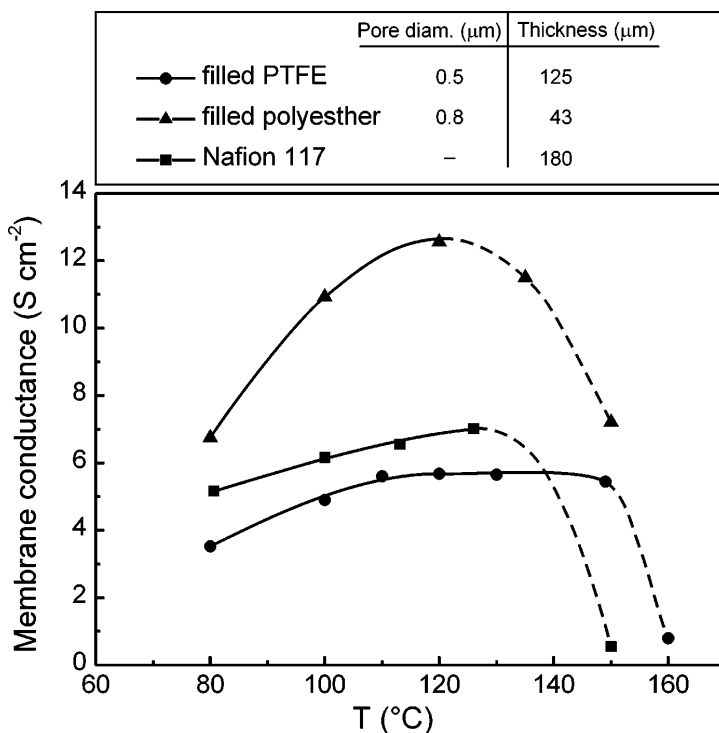


Figure 7 Some recent results on the proton conductivity (95% relative humidity) for porous polymeric membranes filled with the layered zirconium phosphonate composition: $\text{Zr}(\text{O}_3\text{P}-\text{OH})(\text{O}_3\text{P}-\text{C}_6\text{H}_4\text{SO}_3\text{H}) \cdot n\text{H}_2\text{O}$.

particles (see Figure 8). Unfortunately, no TEM images of these filled membranes are available at the moment.

These first results are very encouraging for use at temperatures lower than 100°C because membranes of comparable characteristics with Nafion, but less expensive, could be industrially prepared. Furthermore, because teflon is thermally more resistant than Nafion, the use of these filled membranes in the temperature range $130\text{--}160^\circ\text{C}$ is also very attractive.

SOME GENERAL CONSIDERATION ON PROTON-CONDUCTING COMPOSITE MEMBRANES

The hope of overcoming some of present bottlenecks of PEM fuel cell development by replacing pure proton-conducting membranes with composite membranes explains the interest reserved for this type of membranes and the great number of papers and patents recently published. However, the pressing need for rapidly

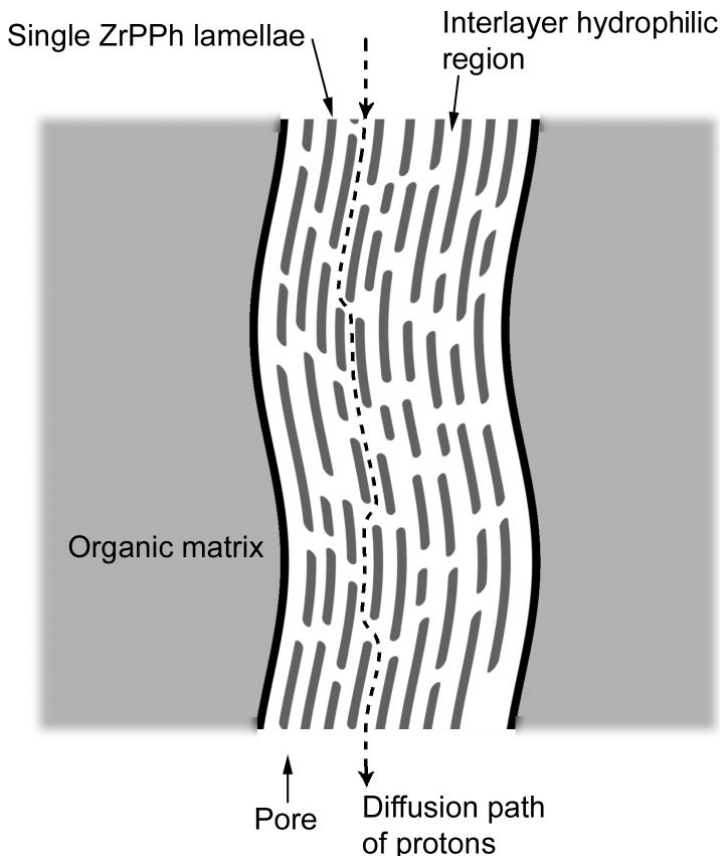


Figure 8 A schematic representation in which the layered zirconium phosphonate particles inside the membrane are formed parallel to the pore surface. This orientation increases the proton conductivity in the direction perpendicular to the membrane, thus minimizing the decrease owing to longer paths of diffusing hydrated protons inside the tortuous pores.

obtaining the results of technological interest has stimulated many researchers and industrial laboratories to go for (often for patent priority reasons) quick attempts at preparation and characterization of composite membranes, and then stopping if the practical results were not as good as expected. There is suspicion by some that some negative results and even the exact know-how of some positive results have not been published. Systematic and comparative research on the effects of structure, crystallinity degree, size, orientation, distribution, etc., of the various types of added particles are therefore rare or lacking. Thus although many types of inorganic particles and different ionomers have been investigated, a definitive conclusion based on unambiguous experimental data cannot yet be drawn

for proton-conducting membranes. Nevertheless, we attempt below to make some comparison among the results obtained in various laboratories in order to establish if some partial conclusion can be made and if some of the expected technological requirements can be really fulfilled with these membranes.

As far as ionomers of low-proton conductivity are concerned, the most impressive results in terms of conductivity improvement were reported for sulfonated polysulfone filled with $\text{H}_3\text{Sb}_3\text{P}_2\text{O}_{14}$ and for s-PEK membranes filled with zirconium phosphonates. For ionomers of very-high-proton conductivity, such as perfluorinated polymers bearing $-\text{SO}_3\text{H}$ groups, the filling with ZrP, silica, or heteropolyacid nano-particles has a positive effect on fuel cell performance at temperatures higher than $90\text{--}100^\circ\text{C}$, even for relative humidity considerably lower than 100%. This effect cannot be simply connected to an increasing number of proton carriers or to specific proton acceptor properties of the inorganic particles, since silica particles have negligible proton conductivity, whereas $-\text{Si-O-Si-}$ and $-\text{Si-OH}$ groups are expected to be better proton acceptors than $-\text{O}_3\text{POH}$ groups. On the other hand, the explanation that these hydrophilic compounds behave as water reservoirs is, in our opinion, not very convincing. It is known that $\alpha\text{-ZrP}$ has only one water molecule for every two $\text{O}_3\text{P-OH}$ groups. In any case, under fuel cell conditions, the proton diffuses toward the cathode with one or more water molecules (65) so it is evident that the original water reservoir is emptied rapidly if no water is supplied with humidified gas and/or by back-diffusion of the water produced at the cathode. On the other hand, no clear experiments on the effect of added hydrophilic particles on the water back-diffusion are presently available. Thus the notion that these hydrophilic particles replace the loosely bonded water within the hydrophilic Nafion domains seems to be, at the moment, the most plausible explanation. In our opinion, water interacting with the surface of the filler is more likely to be retained than loosely bonded water in unmodified Nafion, but still mobile enough to allow for fast proton transport. This leads to the conclusion that, opposed to what is commonly believed, moderately hydrophilic fillers should be more efficient in the temperature range $80\text{--}130^\circ\text{C}$ than strongly hydrophilic fillers.

In addition, the mechanical reinforcement of the membrane, and hence the reduction of the swelling properties, could also play an important role, especially in the temperature range $90\text{--}110^\circ\text{C}$, where high humidification conditions can be still obtained at acceptable pressures of the cell.

The second consideration is that the properties of the modified membranes have frequently been tested in the wrong temperature and relative humidity ranges, or their application has been attempted for unsuitable PEM fuel cell types. Although many insoluble and stable inorganic particles dispersed in a variety of ionomeric matrices have been considered, seldom have the structure, crystallinity degree, shape and dimensions of the particles, as well as their distribution in the various domains of the hydrated ionomers, been thoroughly investigated. In addition, this could explain the many apparent discrepancies between the results obtained in the various laboratories, even with the same type of inorganic particles. For example, consider composite membranes containing particles of $\alpha\text{-ZrP}$, which

are presently among the most investigated composite membranes. Even limiting our attention to only three typical proton-conducting ionomers (e.g., Nafion, s-PEK, and s-PSU), the number of possible nano- and micro-composite membranes is still very large because, as seen before, this layered compound can be inserted (*a*) as powdered preformed particles, (*b*) as preformed exfoliated lamellae, (*c*) by in situ formation in the ionomer solutions, and (*d*) by in situ precipitation in preformed membranes of the pure ionomer. Furthermore, for each type of the above composite membranes, the properties are strongly influenced by the particle content, particle size, distribution and orientation of the exfoliated particles, and exfoliation degree. Finally, in each type of the above membranes ZrP can be replaced by a large number of its organic derivatives, thus obtaining a large number of additional composite membranes with different properties. Therefore, it is evident that comparisons among this large number of composite membranes are difficult. Even some results obtained in the same laboratory could appear in contradiction if the influence of preparation method, size, and orientation of the particles is not carefully taken into account (see for example *curves a* and *b* of Figure 4). It is also clear that future research on these composite membranes must be less dispersive and essentially related to the desired fuel cell applications of the composite membrane and/or to the particular technological obstacle that we wish overcome.

For example, if the use of the composite ionomer-ZrP membrane is confined to direct methanol fuel cells, it will be necessary to overcome the large methanol crossover of pure ionomer membrane. As schematically shown in Figure 9, the exfoliation degree, the size, the homogeneous distribution, and the orientation of the exfoliated particles assume particular importance. Thus incorporation of preformed well-exfoliated ZrP particles in the ionomer solution, followed by casting, should be the best preparation method. In this case, the size of the particles can be chosen; large polylamellar aggregates can be avoided as the casting procedure favors the orientation of the lamellar particles parallel to the membrane surfaces. Note that, due to the increased length of the transport pathway, a concomitant lowering of the proton conductivity must be also expected. The insertion of exfoliated derivatives of ZrP exhibiting greater proton conductivity could offset this problem.

If hydrogen or indirect methanol fuel cells operating at temperatures higher than 90–100°C are desired, particular attention should be given, for example, to the methods based on in situ formation of ZrP, or its derivatives, in organic solutions of Nafion or in preformed Nafion membranes. The partial replacement of pore water with α -ZrP particles could also be beneficial in order to reduce membrane dimensional changes under dehydrating conditions. In the absence of filler, the collapse of the hydrophilic domains upon dehydration is also expected to damage the triple contact between electronic conductor, catalyzer, and proton conductor inside the fuel cell's porous electrodes. These considerations agree with the fact that the modification of the active layer of the electrodes by incorporation of Nafion filled with silica or ZrP phosphonates is already sufficient to improve the performance of fuel cells based on commercial Nafion membranes above 100°C (66).

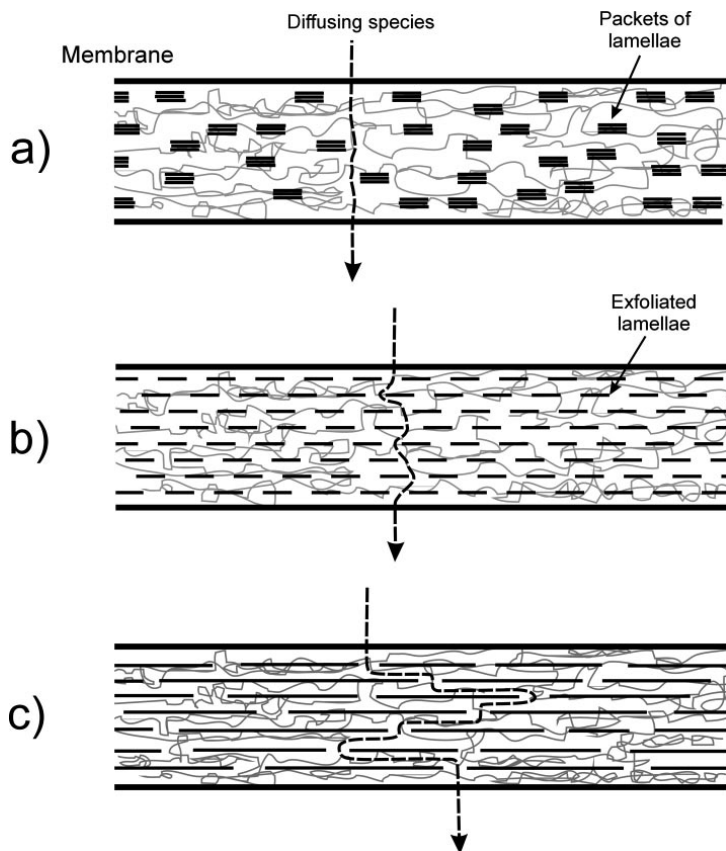


Figure 9 Schematic view of a hybrid ionomeric membrane containing oriented lamellae of ZrP. The increase of the tortuous path encountered by a given diffusing species with increasing degree of exfoliation and/or size of lamellar particles is also shown.

Considerations similar to those above reported for layered α -ZrP could be made for composite membranes containing other inorganic fillers. The preparation of composite membranes filled with silica or hydrous metal oxides could also take advantage of the use of soluble precursors in organic solvents such as the alkoxides. On the other hand, the negligible proton conductivity of silica can be a serious disadvantage at high-filler loading, whereas the reduction of the methanol crossover should be lower than that expected for oriented lamellar particles of zirconium phosphate.

Finally, if the goal is that of preparing more economical membranes than Nafion for hydrogen fuel cells operating at temperatures lower than 100°C, the attention should be directed to low-cost ionomers filled with high contents of particles

exhibiting high conductivity. As seen above, the preparation of s-PEEK or s-PEK membranes filled with superacid zirconium phosphonates is promising.

Economical membranes could be also obtained using porous polymeric membranes filled with ZrP derivatives exhibiting proton conductivity higher than $10^{-2} \text{ S cm}^{-1}$. Recent results obtained in our laboratory are indeed encouraging.

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LITERATURE CITED

1. Rikukawa M, Sanui K. 2000. *Prog. Polym. Sci.* 25:1463–502
2. Sone Y, Ekdunge P, Simonsson D. 1996. *J. Electrochem. Soc.* 143:1254–59
3. Bregman JI, Braman RS. 1965. *J. Colloid Sci.* 20:913–22
4. Alberti G. 1975. In *Semaine sur la thème Membranes Biologiques et Artificielles et la Desalination de l'eau*, ed. R Passino, pp. 629–69. Città del Vaticano: Pontificia Acad. Sci.
5. Alberti G, Casciola M, Costantino U, Levi G. 1978. *J. Membr. Sci.* 3:179–90
6. Alberti G, Casciola M, Costantino U. 1983. *J. Membr. Sci.* 16:137–49
7. Alberti G. 1986. In *Membranes and Membrane Processes*, ed. E Drioli, M Nakagaki, pp. 461–73. New York: Plenum
8. Alberti G, Costantino U, Palombari R. 1989. *Proc. First Int. Conf. Inorganic Membranes*, ed. L Cot, J Charpin, pp. 25–30. Languedoc-Rousillon, France
9. Alberti G. 1992. In *Membranes*, ed. Dept. Sci. Tech., pp. 295–311. New Delhi: Oxford & IBH
10. Rozière J, Jones DJ, Tchicaya-Bouckary L, Bauer B. 2002. *Int. Patent No. WO 0205370*
11. Alberti G, Casciola M, Costantino U. 1985. *J. Colloid Interface Sci.* 107:256–63
12. Alberti G, Dionigi C, Giontella E, Murcia Mascaros S, Vivani R. 1997. *J. Colloid Interface Sci.* 188:27–31
13. Alberti G, Casciola M, Pica M, Jones DJ, Rozière J, Bauer B. 2002. *Italian Patent No. PG2002A0013*
14. Grot W, Rajendran G. 1996. *Int. Patent No. WO 96/29752*
15. Mauritz KA, Warren RM. 1989. *Macromolecules* 22:1730–34
16. Alberti G, Casciola M, Pica M. 2002. *Italian Patent No. PG2002A0015*
17. Clearfield A. 1998. In *Progress in Inorganic Chemistry*, ed. KP Karlin, 47:373–507. New York: Liss
18. Alberti G, Bein T, eds. 1996. *Comprehensive Supramolecular Chemistry*, Vol. 7. Oxford, UK: Pergamon. 837 pp.
19. Casciola M, Marmottini F, Peraio A. 1993. *Solid State Ionics* 61:125–29
20. Alberti G, Boccali L, Casciola M, Massinelli L, Montoneri E. 1996. *Solid State Ionics* 84:97–104
21. Alberti G. 1961. *Atti Acc. Naz. Lincei. Rend.* 31:427–28
22. Alberti G, Conte A, Torracca E. 1963. *Atti Acc. Naz. Lincei. Rend.* 35:548–54
23. Murphy OJ, Cisar AJ. 1998. *U.S. Patent No. 6,059,943*
24. Mauritz KA, Stefanithis ID. 1990. *Macromolecules* 23:1380–88
25. Stefanithis ID, Mauritz KA. 1990. *Macromolecules* 23:2397–402
26. Mauritz KA, Stefanithis ID, Davis SV, Scheetz RW, Pope RK, et al. 1995. *J. Appl. Polymer Sci.* 55:181–90
27. Gummaraju RV, Moore RB, Mauritz KA. 1996. *J. Polym. Sci. B.* 34:2383–92
28. Mauritz KA. 1998. *Mater. Sci. Eng. C* 6: 121–33
29. Baradie B, Dodelet JP, Guay D. 2000. *J. Electroanal. Chem.* 489:101–5

30. Apichatachutapan W, Moore RB, Mauritz KA. 1996. *J. Appl. Polym. Sci.* 62:417–26
31. Shao PL, Mauritz KA, Moore RB. 1995. *Chem. Mater.* 7:192–200
32. Zoppi RA, Yoshida IVP, Nunes SP. 1997. *Polymer* 39:1309–15
33. Zoppi RA, Nunes SP. 1998. *J. Electroanal. Chem.* 445:39–45
34. Wang H, Holmberg BA, Huang L, Wang Z, Mitra A, et al. 2002. *J. Mater. Chem.* 12:834–37
35. Watanabe M, Uchida H, Seki Y, Emori M, Stonehart P. 1996. *J. Electrochem. Soc.* 143:3847–52
36. Watanabe M, Uchida H, Emori M. 1998. *J. Electrochem. Soc.* 145:1137–41
37. Antonucci PL, Aricò AS, Creti P, Ramunni E, Antonucci E. 1999. *Solid State Ionics* 125:431–37
38. Aricò AS, Antonucci V. 1999. *Eur. Patent No. EP 0926754A1*
39. Bonnet B, Jones DJ, Rozière J, Tchicaya L, Alberti G, et al. 2000. *J. New Mater. Electrochem. Systems* 3:87–92
40. Jones DJ, Rozière J. 2003. In *Handbook of Fuel Cells—Fundamental, Technology and Applications*, ed. W Vielstick, U Gasteiger, A Lamm. New York: Wiley & Sons. In press
41. Nunes SP, Ruffmann B, Rikowski E, Vetter S, Richau K. 2002. *J. Membr. Sci.* 203:215–25
42. Savadogo O. 1992. *J. Electrochem. Soc.* 139:1082–87
43. Savadogo O. 1992. *Electrochim. Acta* 37:1457–59
44. Nakamura O, Ogino I, Kodama T. 1981. *Solid State Ionics* 3-4:347–51
45. Malhotra S, Datta R. 1997. *J. Electrochem. Soc.* 144:L23–26
46. Tazi B, Savadogo O. 2000. *Electrochim. Acta* 45:4329–39
47. Tazi B, Savadogo O. 2001. *J. New Mater. Electrochem. Systems* 4:187–96
48. Zaidi MJ, Mikhailenko SD, Robertson GP, Guiver MD, Kaliaguine S. 2000. *J. Membr. Sci.* 173:17–34
49. Honna I, Takeda Y, Bae JM. 1999. *Solid State Ionics* 120:255–64
50. Honna I, Nomura S, Nakajima H. 2001. *J. Membr. Sci.* 185:83–94
51. Staiti P, Minutoli M, Hocevar S. 2000. *J. Power Sources* 90:231–35
52. Staiti P, Freni S, Hocevar S. 1999. *J. Power Sources* 79:250–55
53. Staiti P, Minutoli M. 2001. *J. Power Sources* 94:9–13
54. Staiti P. 2001. *J. New Mater. Electrochem. Systems* 4:181–86
55. Staiti P, Aricò AS, Baglio V, Lufrano F, Passalacqua E, Antonucci V. 2001. *Solid State Ionics* 145:101–7
56. Deniard-Courant S, Piffard Y, Barboux P, Livage J. 1988. *Solid State Ionics* 27:189–94
57. Baradie B, Poinsignon C, Sanchez JY, Piffard Y, Vitter G, et al. 1998. *J. Power Sources* 74:8–16
58. Genova-Dimitrova P, Baradie B, Foscallo D, Poinsignon C, Sanchez JY. 2001. *J. Membr. Sci.* 185:59–71
59. Costamagna P, Yang C, Bocarsly AB, Srinivasan S. 2002. *Electrochimica Acta* 47:1023–33
60. Yang C, Srinivasan S, Aricò AS, Creti P, Baglio V, Antonucci V. 2001. *Electrochem. Solid-State Lett.* 4:A31–34
61. Jones DJ, Rozière J. 2001. *J. Membr. Sci.* 185:41–58
62. Tchicaya-Bouckary L, Jones DJ, Rozière J. 2002. In *Fuel Cells—from Fundamentals to Applications*, 2:40–45. New York: Wiley
63. Alberti G, Costantino U, Casciola M, Ferroni S, Massinelli L, Staiti P. 2001. *Solid State Ionics* 145:249–55
64. Yeager HL, Steack A. 1981. *J. Electrochem. Soc.* 128:1880–84
65. Zawodzinski TA, Davey J, Valerio J, Gottesfeld S. 1995. *Electrochim. Acta* 40:297–302
66. Alberti G, Casciola M, Ramunni E, Ornelas JR. 2002. *Eur. Patent No. EP1205994*