Macromol. Symp. ***138****, 85–91 (1999)*

Water Sorption and Protonic Conductivity in a Filled/Unfilled Thermostable Ionomer for Proton Exchange Membrane Fuel Cell

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SUMMARY: A filled ionomeric membrane is achieved by dispersing several % in weight of the phosphatoantimonic acid $H_3Sb_3P_2O_{14}$, xH_2O (H3), in a Sulfonated PolySulfone (SPS) solution [1]. Water up-take of pristine and filled SPS of different cation exchange capacity (cec) was measured at 25°C and 80°C : it is higher for filled than unfilled membrane. Comparatively, protonic conductivity measurements performed on the same samples show a higher conductivity for the filled samples than for the unfilled. The conductivity value is higher than that expected from the overall calculated concentration in charge carriers: a conductivity value of 0.06 $S.cm^{-1}$ is gained at 80°C under 100% Relative Humidity (HR) for a 1.4 $meq.g^{-1}$ cec SPS filled with 8% in H3.

Introduction

For the last two decades, the demand of electrical power sources has doubled every three years. It particularly concerns electrochemical devices such as light, quickly rechargeable batteries for portable electrical devices and high energy density batteries as well as autonomous powerful fuel cells (FC) for electrical vehicles. The main advantage of fuel cells resides in the fast recharge process which consists in replacing the hydrogen bottle or filling the methanol tank when hydrogen comes from methanol reforming.

Both harness a chemical reaction to generate electrical energy. This conversion process occurs thanks to the redox character of the reactions at each electrode. An electronic insulator (the electrolyte and/or the separator) is placed between the electrodes and obliges the electron flux to go from one electrode to the other throughout the external circuit of the battery (fig.1). Inside the cell, the electrical circuit is completed by the ionic transport through the liquid electrolyte and the separator or through a solid state electrolyte (polymeric or inorganic).

The battery electrode materials are metals or insertion materials whereas those of fuel cells are gas. Fuel Cells are capable of providing electricity from the reaction between hydrogen

CCC 1022-1360/99/$ 17.50+.50/0

(and natural or coal gas) and atmospheric oxygen. According to the electrolyte, which imposes the running temperature, the following names are currently used[2]:

> AFC - Alkaline Fuel Cells (65°C), PEMFC - Proton Exchanger Membrane Fuel Cells (70- 80°C)°C. PAFC - Phosphoric Acid Fuel Cells (190°C), MCFC - Molten Carbonate Fuel Cells (300°C), SOFC - Solid Oxide Fuel Cells (600-1000°C).

Due to its running temperature and its power density PEMFC appear as a well adapted system for electrical vehicles. PEMFC may be fuelled on the one hand by pure oxygen or air on the other hand by pressurised or methanol reformed hydrogen and run around 80°C. The elementary cell consists of two electrodes separated by the proton-conducting polymer membrane (fig 1). The electrodes are made of carbon tissue supporting a fine dispersion of nanometric Platinum particles. Anodic hydrogen oxydation at the anode provides one e$^-$ and H$^+$, the latter crossing over the polyelectrolyte membrane to recombine with atomic oxygen generated from O_2 at the cathode. The reaction produces water, whereas the electron goes in the outer circuit. The stack of decades of the elementary membrane-electrode assembly (m.e.a) leads to the fuel cell. The FC power depends on the catalyst efficiency, the membrane protonic conductivity and on the number of stacked m.e.a.

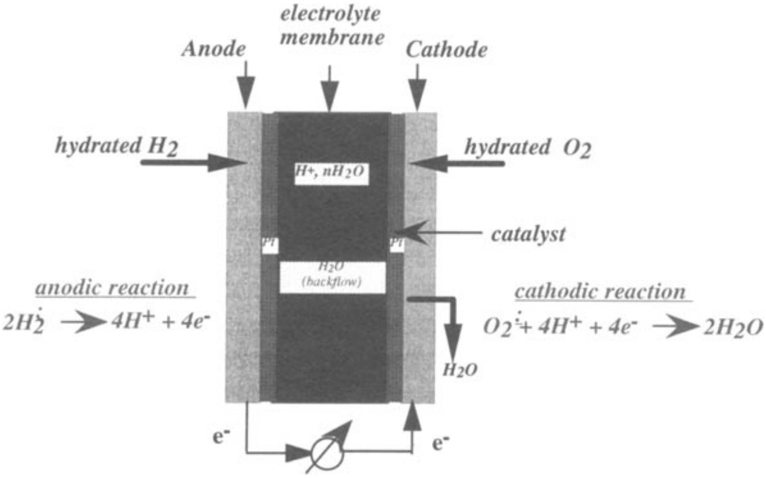


Fig 1 : Basic structure of a PEM fuel cell running at 80°C and electrochemical reactions taking place in the electrodes.

Great improvements have been made during the last five years namely (i) in the minimisation of the electrode based on noble metals (Pt/Ru alloys) (ii) in the bipolar plate thickness sandwiched between the m.e.a stacks (iii) in the overall volume of fuel cells leading to 30kW devices (approximately 200 liters). PEMFC equip several electrical car prototypes and they could soon be commercialised after a drastic reduction in the component costs, in particular that of membranes.

Most research teams used perfluorinated ionomers as PEMFC membranes i.e Nafion® 112 and 117 from Dupont^3). Nafion®, which consists in tetrafluoroethylene $(\text{-CF2-CF2-})_n$ backbone with dangling sulfonated perfluoro ether moieties, has a wide redox stability window and a long life time. As protonic conductivity is ensured by a vehicular mechanism, the acidic proton being carried as H_3O^+ ^4), the membrane conductivity strongly depends on water content ^5). A high dissociation rate may be expected from the hydrophilic superacid groups of Nafion. Their hydrophilicity associated to the hydrophobic character of the teflon backbone allows high current density to be obtained, while maintaining good mechanical properties. Indeed the main drawback lies in their price, related to the syntheses of perfluorosulfonated polymers.

The cost reduction of PEMFC membranes has generated active research in the field of polymeric and composite membranes ^6,7). The main difficulty is to reach, at 80°C, the Nafion conductivity's while keeping the electrochemical, thermal and mechanical properties of the commercial ionomer. In particular a high ionic concentration results in a conductivity increase but induces generally, at the operating temperature of PEMFC (80°C°), a dissolution of the membrane or at least an excessive swelling. In this paper a membrane based on a thermoplastic polyelectrolyte filled by an inorganic material is proposed. In order to use a moderate sulfonation rate, while keeping a high water content, we selected as an inorganic acidic filler $H_nSb_nP_2O_{(3n+5)}$, xH_2O (n = 3) abbreviated as H3. A moderate polyelectrolyte capacity avoids an excessive water swelling, while H3 is expected to maintain a high water content in the membrane.

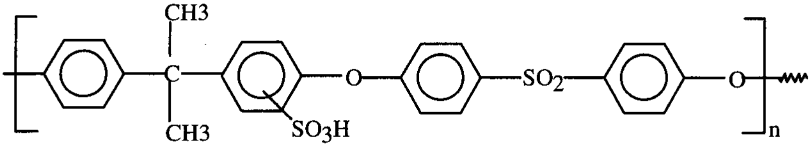
Experimental

TGA measurements were performed on a NETZSCH STA 409 analyser, under helium flow for PSF, and Argon flow for PSS and PSSNa, from ambient temperature to 600 ° C at 10K/min. Conductivity measurements were performed under controlled temperature and relative humidity by impedance spectroscopy using a 4192A Hewlett Packard Impedance meter monitored by a 9340 HP computer driven by a self made program.

Material

The ionomer is obtained by sulfonation of a commercially available polysulfone 8) (Udel provided by Amoco) of Mw=51,000 and Mn=31,000 molecular weight with trimethylsilylchlorosulfonate leading to cation exchange capacity (cec) from 0.8 to 2.5 meq/g. The phosphatoantimonic acid $H_nSb_nP_2O_{(3n+5)}$, xH_2O (n = 3)9) is an inorganic acid consisting of Sb_2O_3 octahedra layers sharing common edges with six phosphates tetrahedra pointing the free edge which carries the acidic proton in the interlamellar space. H3 exhibits some similarities with smectite clays, swelling in water to give a gel. In addition H3 is a rather strong acid 8,9) whose cationic exchange capacity cec reaches 4.3 meq.g^{-1} and provides high protonic conductivity : 0.02 S.cm^{-1} at 25° C under 100% relative humidity (RH)10).

In addition to the technical specifications of the membrane, a low to moderate cost is required as well as the possibility to manufacture the polymer. For this reason we have selected a thermostable "technical" thermoplastic - polysulfone - manufactured by several companies such as Amoco and BASF. Sulfonation, a well-known industrial process, enables the incorporation of ionic functions on the aromatic rings. Fig 2 presents the chemical formula of SPS[1].



Bisphénol-A Polysulfone Sulfoné (PSS)

Fig 2 : extended formula of bisphenol A sulfonated polysulfone (SPS).

Results and discussion

Sulfonated polysulfone

Thermal stability of SPS1) , in Argon, is observed up to 245 ° C where a first weight loss occurs, assigned to sulfonic group elimination 11-13). A second weight loss is observed at 450°C corresponding to the polymeric backbone degradation identified by Rose 14) (Fig 6 in 1)).

Fig.3 shows the variation of water swelling with sulfonation rate at 25 and 80°C and water swelling of 1.28 cec filled SPS. For unfilled SPS water content associated to sulfonic group ranges from 4% for a 0.76 meq.g^{-1} cec to 30% for a 1.4 meq.g^{-1} cec at 25° C. At 80°C the ionomer becomes soluble for cec higher then 1.2 meq/g.

Sulfonated PolySulfone filled by H3

Water uptake of different cec SPS filled with 8% of H3 was measured at 25°C and 80°C. Fig. 3 exemplifies the influence of H3 filling on the water uptake of a 1.26 cec SPS membrane, which goes through a maximum for 8% in H3 weight. Water content associated to hydrophilic group ranges from 20% for the pristine SPS to 35 % at 25° C. At 80°C the water content of the filled SPS is 57 % but at this temperature the filled membrane preserves its dimensions whereas pure equiconductive SPS solubilizes.

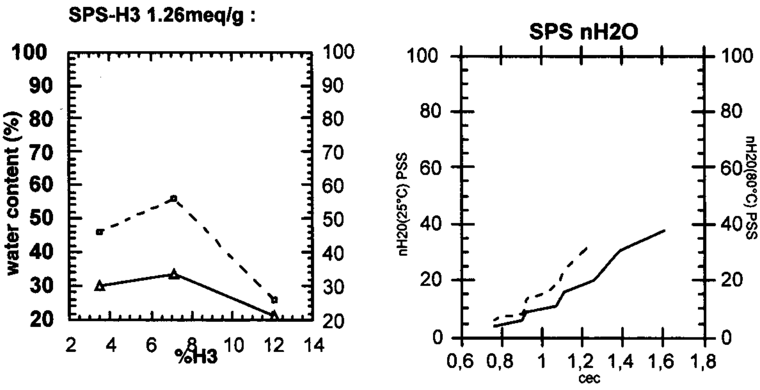


Fig. 3 : SPS and H3-SPS water up-take at 25°C(full line) and 80°C (dotted line).

Protonic conductivity of SPS and SPS -H3

A comparison of the protonic conductivity measurements performed on filled and unfilled SPS shows, at the same sulfonation rate, a clear conductivity increase upon filler addition. Indeed the conductivity is roughly trebled after H3 incorporation. (Fig 4). Moreover the filled samples exhibit a higher conductivity than expected from the overall calculated concentration in charge carriers. From fig. 3 & 4 it appears that H3 increases both the water adsorption and the protonic conductivity σ_{H+}. This conductivity maxima is reached for a rather low H3 loading (8% in weight 1)) and seems to be related to the higher hydrophilicity of the filled membrane. These conductivity values are now very close to those of Nafion (in the same experimental conditions). Obviously, as shown in fig.3, an increase in the sulfonation rate results in an increase in the water up-take in unfilled membranes. Nevertheless for cec values higher than 1.3 meq.g^{-1} the polyelectrolyte becomes at least partially soluble around 80°C. The synergy observed by filling the polyelectrolyte with H3 cannot be only related to an increase in cec. In addition, based on the comparison between the pKa values, the acidity of H3 in water is lower than that of aromatic sulfonic acids. Research is now in progress to understand the conductivity mechanisms in filled membranes and the real function of these fillers.

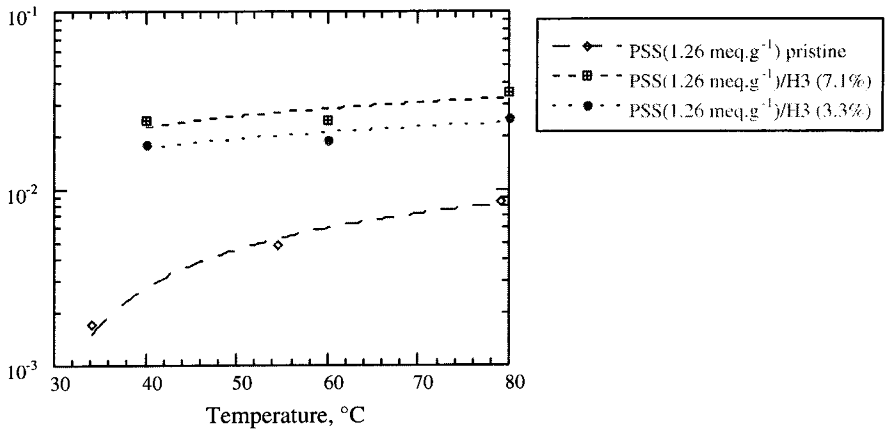


Fig. 4 : conductivity variations at 25°C and 80°C of SPS and H3-SPS.

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