

## ELABORATION AND CHARACTERIZATION OF NAFION AND COMPOSITES MEMBRANES BASED ON PHOSPHATOANTIMONIC ACID

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**ABSTRACT:** Composites membranes based on Nafion blended with Phosphatoantimonic acid (H3) exhibit high conductivities associated to enhanced thermo-mechanical performances as compared to Nafion. The preliminary tests performed on membrane electrode assembly (MEA) based on these composites membranes allowed for a given content in H3 i.e. 10% obtaining improved polarization curves as compared to the pristine membranes.

**Keywords:** Nafion 117®; Composites membranes; Phosphatoantimonic Acid; Mechanical reinforcement; PEMFC; Polarization curves.

### 1. INTRODUCTION

Proton conducting membranes for PEMFCs are usually based on thin ionomer films. The membrane separates the electrodes, allows proton transportation from anode to cathode and creates a barrier against the passage of gases or fluids (e.g. methanol). However, the ionomer itself does not provide any appreciable conductivity. The membrane must therefore be swollen by molecules, e.g. water, to ensure proton conductivity. Water uptake by the membrane is therefore one of the essential parameters in obtaining high conductivity levels. Indeed, due to its high dielectric constant, water favours dissociation of the ion-pair, increasing the concentration of charge carriers and the solvation of both anion and proton.

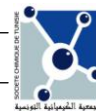
Generally, two principal mechanisms are used to describe proton diffusion through the membranes [1, 2].

One is the vehicle mechanism whereby a proton combines with vehicles such as  $H_3O^+$  where the conductivity is directly dependent on the rate of vehicle diffusion. The other is the Grotthus mechanism (hopping) whereby protons are transferred from one proton acceptor site to another by hydrogen bonds. In this mechanism, additional reorganization of the proton environment, consisting of reorientation of individual species or even more extended ensembles, leads to the formation of an uninterrupted trajectory for proton migration.

But it is important for PEMFC development to focus on developing a PEM (Proton Exchange Membrane) which has satisfactory proton conductivity at higher temperatures (above 100°C) and/or low relative humidity [3-5] because cells that can operate in such conditions have a number of advantages over lower temperature cells. However, at temperature higher than 100°C the water evaporate and the membrane conductivity decreases drastically.

An effective way to achieve low-humidity and high-temperature operation of Ionomers membranes is to elaborate the hygroscopic inorganic/organic composite membranes, in which the ionomer or generally the polymer is blended with hydroscopic inorganic particles.

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The hygroscopic solid inorganic proton conductors are suitable membrane fillers for increasing the number of protonic carriers and thus improving the hydrophilic character of the membranes.

Among the inorganic solid proton conductors [6-8] zirconium phosphates, heteropolyacids, metal hydrogen sulfate and a few others are of special interest for developing high temperature composite membranes for PEMFCs.

Blending a sulfonated polyethersulfone with 2 highly hygroscopic fillers an acidic one, the Phosphatoantimonic Acid (H3) and a fairly neutral one i.e. clay [9] we observed, in the LEPMI laboratory, that despite similar water uptakes the former led to higher conductivities. It was therefore inferred that H3, which is a strong solid inorganic acid [10, 11], contributes by its acidic protons to the overall conductivity of the composite membrane. As the PFSA (Perfluorosulfonic Acid) IECs are much lower a too huge water uptake must not be feared. Conversely, it is well known that due to their hydrophobic perfluorinated backbone, membranes based on PFSA ionomers suffer hydration problems above 80-90°C [12-20].

This contribution reports the effect of H3 fillers on Nafion Performances. We must emphasize that many papers deal with the use of composite PFSA membranes [3, 21-25] but, to the best of our knowledge they did not report on H3 composites. As H3 has outstanding stability and intrinsic conductivity performances, we selected this inorganic material to focus on Nafion-H3 composite membranes. This has required developing a reproducible elaboration process paying, in particular, a great attention to the H3 dispersion through the thickness of the composite membrane. The composite membrane performances were assessed by mechanical and physicochemical characterizations i.e. conductivity and XRD diffractions as well as SEM analyses to check the homogeneous dispersion of the fillers through the composite membranes. Last, membranes electrode assembly (MEAs) were tested using a characterization test bench.

## 2. EXPERIMENTAL PART

### 2.1 The composite membranes

The Nafion 117 supplied by Aldrich® was dissolved according to the following procedure. 12 g of Nafion film was cut in small pieces and then immersed in 2M LiOH aqueous solution in order to transform the  $\text{SO}_3\text{H}^+$  function into  $\text{SO}_3\text{Li}^+$  one (neutralized Nafion). After 12h, the neutralized Nafion was washed with deionized water up to neutral pH. Then the neutralized Nafion was transferred into a stainless steel reactor vessel containing 120 ml of ethanol/water mixture (50/50 vol/vol). The solution was heated at 250°C at a pressure of 30 Bars for 6 hours. After cooling the solution was filtered through Whatman PTFE filter of 0.2 micron. The filtrate was then freeze dried at -110°C for 12 hours. The resulting Nafion powder was treated with 2M aqueous nitric acid solution to regenerate the  $\text{SO}_3\text{H}^+$  function. After filtration and washing with deionized water until neutral pH, the acidic Nafion powders are dried for 12 hours at 80°C under vacuum.

### Membrane elaboration

1g of Nafion (acidic form) was dissolved in 10 ml dimethylacetamide (DMAc) and inorganic H3 fillers were added. In order to well disperse the H3 fillers, the mixture was placed on ultrasound bath. The obtained viscous solution was then casted into a Petri dish and was heated at 80°C in an oven for 2 days to evaporate the solvent.

Afterwards, the membrane was heated at 150°C for 1 hour. Then, the membrane was removed from the Petri dish, treated in a 2M boiling aqueous solution of nitric acid for 1 hour. Then, the membrane was washed in deionized water in order to fully remove nitric acid.

After drying, the thickness of the membrane was about 80 +/- 5µm.

### 2.2 Dynamic Mechanical Analyses (DMA)

The measurements were carried out using a DMA Q 800 spectrometer from TA instrument working in the tensile mode, the strain amplitude was fixed at 0.05% well below the limit of the linear viscoelastic regime.

Measurement of the tensile storage modulus  $E'$  was performed in isochronal condition (1Hz) and the temperature was varied between 20°C and 250°C using a temperature ramp of 2°C.min<sup>-1</sup>.

### 2.3 Conductivity measurements

The membranes were sandwiches between two stainless steel electrodes. Impedances were determined by electrochemical impedance spectroscopy using a Hewlett Packard 4192A spectrometer in the frequency range 5MHz – 13MHz. The measurements were performed from 20°C to 90°C at a constant relative humidity of 95%. The temperature was equilibrated for 12 hours before each measurement.

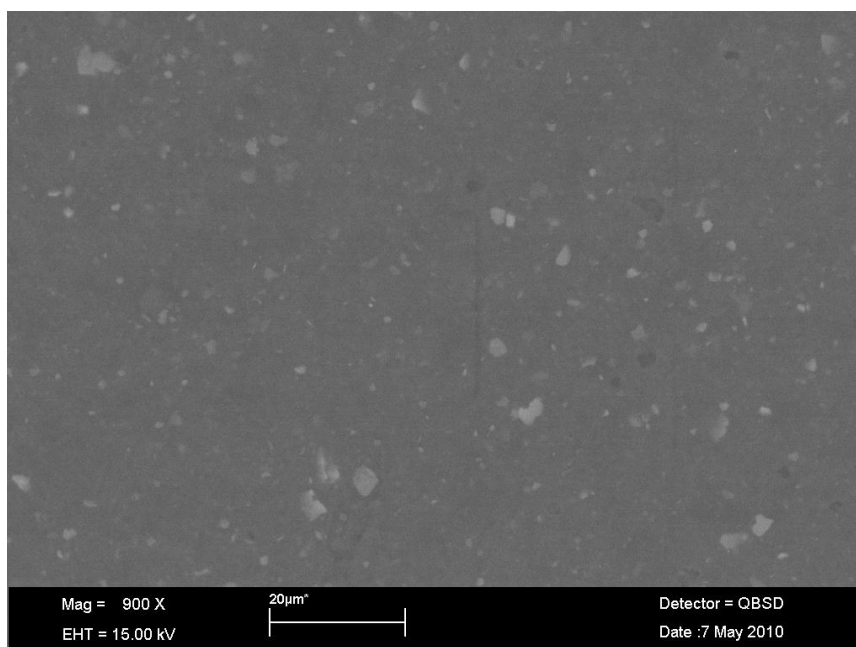
### 2.4 Polarization curves

Considering the polarisation curves, we used a cell Paxitech of 5\*5 coupled to a biologic FCT-50S. The MEA polarization curves were performed under the following conditions: gas stoichiometry H<sub>2</sub> (1.2), O<sub>2</sub> (1.6) and gas flows: H<sub>2</sub> (120 ml/mn), O<sub>2</sub> (300 ml/mn). Relative pressures: 1 bar both for O<sub>2</sub> and H<sub>2</sub>. Both gases were humidified at 100%. The equilibration time of the membrane was 2 hours, and the time between 2 measurements was 15 min. Potential is applied between the two electrodes from high potential up to low value, followed by a second scan in the opposite direction.

## 3. RESULTS AND DISCUSSION

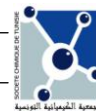
### 3.1 Membrane elaboration

The properties of composite membranes depend not only on the nature of the ionomer and the fillers used but also on the amount, homogeneous dispersion, size, and orientation of the solid particles dispersed in the polymer matrix. Therefore we paid a great attention to avoid the heterogeneous dispersion of H3, using, as detailed in 2.1 the ultrasound bath. Due to the high density of H3 it can be feared that most of the H3 fillers sediment concentrate at the bottom of the membrane during the film casting elaboration process.



**Figure 1: MEB analysis of H3/Nafion composite membrane.**

According to MEB investigations (Fig. 1), the overall repartition of H3 (white spot) within the membrane appears to be homogeneous whereas the size of the H3 particles ranges from 0.5µm to 3µm. One can suggest that, although H3 is insoluble in DMAc, the use of sonification and the relative high viscosity of the starting solution should prevent its sedimentation. In order to put in



evidence the influence of fillers concentration we prepare 3 membranes, one without H3 (Nafion 0) and two containing 10 and 20% H3 in weight respectively (Nafion 10, Nafion 20).

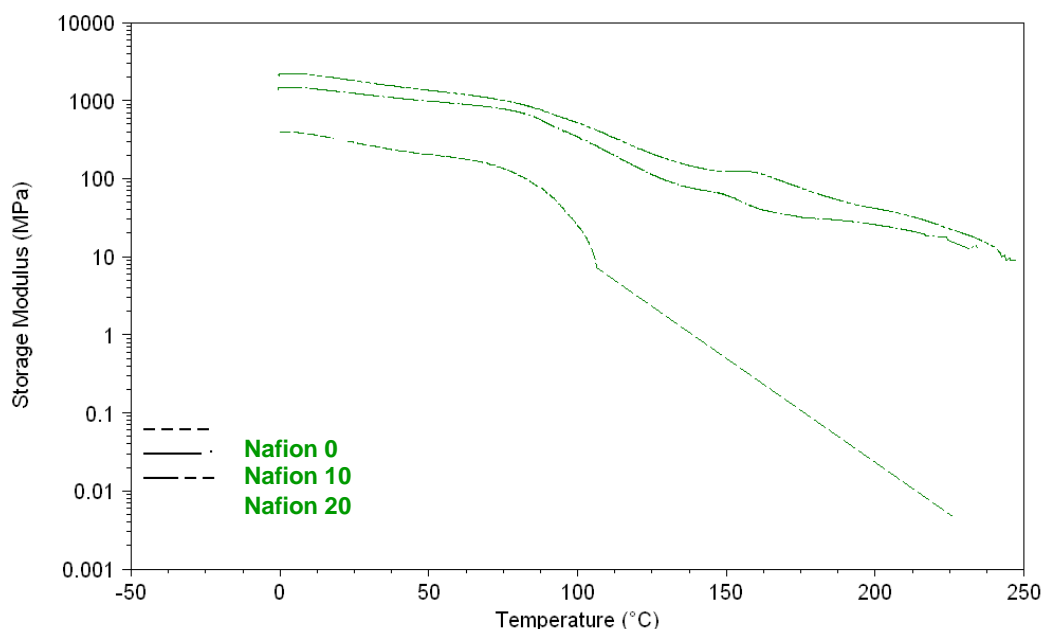
The H3 presents a Rhombohedral structure [26]. XRD experiments have been performed on the composite membrane in view to check if its structure was neither unaffected by sonification nor by the overall film casting process. It has been clearly shown that H3 crystallographic structure remains unchanged allowing the protonic properties of H3 to be retained.

### 3.2 Thermomechanical behaviour

The thermo-mechanical performances of a PEMFC membrane are essential to allow the membrane to be shaped into thin films. The membrane resistivity depends on the membrane thickness. For a membrane possessing good thermo-mechanical properties the thickness can be decreased leading to a lowering of internal resistance (ohmic drop) and implicitly to much better fuel cell performances. The figure 2 presents the evolution of storage modulus versus temperature and it show that the composite membranes (nafion 10 and Nafion 20), exhibit a neat improved storage modulus in the whole temperature range as comparing to Nafion 0. Moreover, this improvement is linked with the amount of H3 within the composite membrane. Table 1 well illustrates this rule. At 110°C the Nafion 0 membrane has a storage modulus close to 5 MPa while for Nafion filled by 10% and 20% H3, storage modulus reach respectively 300 MPa and 450MPa.

**Table I: Membranes Storage Modulus Values**

| Temperature | 110°C   | 150°C   |
|-------------|---------|---------|
| Nafion 0%   | 5 MPa   | 0,3 MPa |
| Nafion 10%  | 300 MPa | 90 MPa  |
| Nafion 20%  | 450 MPa | 200 MPa |



**Figure 2: Storage Modulus of filled and unfilled Nafion Membranes**

Moreover, it should be pointed out that this improvement is also observed at high temperature (i.e. 150°C). Whereas Nafion 0 is completely flowing, the composites membranes have storage modulus higher than 90 MPa. As a matter of fact, one can suggest that this improvement should allow to

decrease significantly the membrane thickness and thus internal resistance. Therefore, a substantial resistivity gain can be expected both from an optimization of filler content and the film casting elaboration

### 3.3 Conductivity data

The conductivities of the composite membranes at different H3 concentrations are compared in Figure 3. The lowest conductivities were obtained with Nafion 0 while for composite membranes their conductivities increase regularly with the H3 content. This behaviour can be explained for a hand by the increase of the membrane ionic exchange capacity due to the presence of H3 and by other hand but a higher ability of the membrane to water uptake. Moreover, the membrane, conductivity is poorly activated in the temperature range 0-75°C.

In addition, taking into account, the high mechanical properties of the composites membranes comparatively to Nafion 0, decreasing the thickness should provide high performance in fuel cell due to decrease of ohmic drop

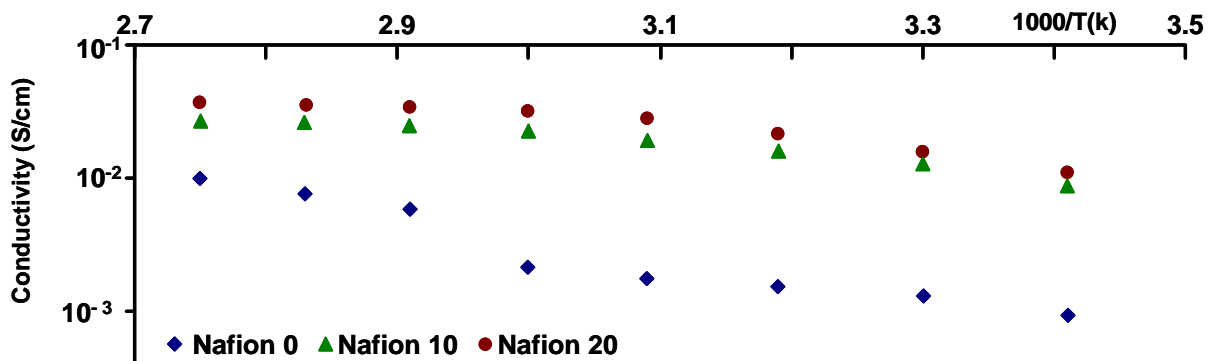


Figure 3: Comparison of the conductivity plots vs. reciprocal temperature (RH=95%)

### 3.4 Polarization Curves

The polarization curves were performed for Nafion 0, and for the membranes filled by 10 and 20% H3 (Fig. 4). In all cases, as expected, along with the increase of current density for the composite membranes, one can distinguish successively activation and ohmic polarization regions.

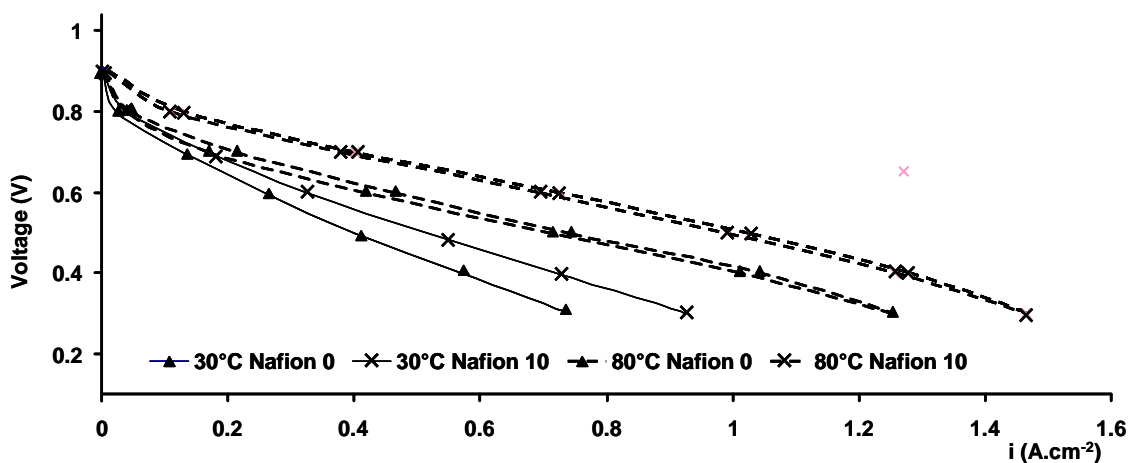
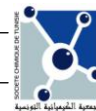


Figure 4: Polarisation Curves under the conditions described in the experimental part

One can observe that the increase the amount of H3 leads to higher current densities. For example, at high temperature, composite membrane (Nafion 10) exhibits, at 0.6 V, a current density of 0.7 A.cm<sup>-2</sup> whereas the Nafion 0% only reaches 0.46 A.cm<sup>-2</sup>.



Since these membranes present close thickness, one can compare the slope of the I/E response in the ohmic polarization region. Along with amount of H3 this ohmic contribution decreases by a factor about 2 comparing to the Nafion 0. This result is in good agreement with the higher conductivity of the composite membrane comparing to Nafion 0. One can suggest that H3 should promote the protonic conduction leading to the improvement of the mass transport in composite membranes.

### Conclusion

This study shows unambiguously that the presence of H3 within the Nafion matrix allows improving both the mechanical and the electrochemical performances of the membrane. Significant mechanical gains are obtained in relation with the content of H3, allowing investigating lower thickness. In parallel, interesting electrochemical results have been obtained demonstrating that H3 contributes to increase mass transport, illustrated by higher current density as compared to the pristine Nafion. Further experiments are in progress, in particular in order to assess the influence of relative humidity of the gases (i.e. O<sub>2</sub> and H<sub>2</sub>) on the electrochemical behaviour.

### Acknowledgment

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