Impact of the SG phase morphology on the performances and durability of hybrid polymer membranes for fuel cell applications

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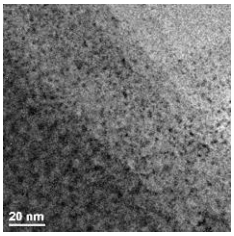
Abstract

Proton-Exchange Membrane Fuel Cells (PEMFC) has emerged as a promising emission-free energy conversion device. However, the ionomer membrane at the heart of the device fails to deliver durable performance (to be achieved: 8000h for transportation, 50000h for stationary) at high temperature (100-150°C vs 80°C for std. Nafion) and low relative humidity (30%RH). The aim of our work is to improve existing membranes (better chemical and thermomechanical stabilities, better conductivities) by Sol-Gel (SG) hybridization. SG precursors are selected to diffuse through commercial membranes and introduce stabilizing organo-functional groups offering either a sacrificial stabilization (consumed over time) or a redox stabilization (regenerable) by degrading oxidizing agents produced during Fuel Cell operation. As the morphology (size, interaction/dispersion, connectivity) and localization (polar/apolar regions) of the SG phase inside the host matrix are parameters expected to be crucial for properties (H^+ conductivity, water uptake), durability (H_2O_2-accelerated aging tests to assess the effectiveness of the reactive SG phase) and performances (FC operation) of the hybrid membranes, we explored their morphology at all relevant length scales. In this purpose, we use a combination of direct space (AFM/SEM/TEM) and reciprocal space (contrast variation SANS/SAXS) techniques (dimensional scale covered: from a hundred to a few nanometers) with regard to the **chemistry of the SG Precursors** (SGPs) (stabilization group, number of hydrolysable functions), yielding a **variety of morphology** (mass fractal structure *vs.* dispersed spherical aggregates *vs.* interconnected ones). H_2O_2-accelerated aging tests and preliminary fuel cell tests show promising operability of the hybrid membranes and the potential of the SG phase to inhibit the chemical ageing of sPEEK. With this work, we are confident to reach a **predictive approach** of the **key parameters governing the final properties**.



TEM image of hybrid membrane with 28.6wt% of SG phase.

Introduction

Proton exchange membranes fuel cells (PEMFCs) are considered as promising power systems due to many attractive features, including high power density, rapid start-up and high efficiency, without emission of any greenhouse gas. Although great advances in the development of PEMFC, membrane degradation under harsh and/or long-term operating conditions is highly detrimental and ultimately causes the system failure. In addition, a higher temperature range (up to150°C) is required in order to mitigate the cooling management for PEMFC applications, increase the tolerance of the catalysts to CO poisoning and reach faster electrochemical reactions. Design of more durable membranes able to operate at higher temperature/low RH is complicated because improving the functional properties (water uptake, conductivity), usually negatively impacts durability and mechanical properties.

Different strategies have been developed to improve both the performances and durability of the membrane for a large-scale implementation of the PEMFC technology, like for example the elaboration of Inter Penetrated Networks (IPN)[1-2], the design of novel block-copolymers[3-6] and the use of fillers/nanocharges and stabilizing additives[7].

For hybrid membranes with nanocharges and stabilizing additives big issues come from their dispersion and their possible migration then elution in water during FC operation. Moreover, the proton conductivity, the mechanical properties and the permeability of the membrane can also be impacted by the presence of these additives.

1. Scientific Approach

Using stabilizing additives against chemical degradation was studied since 2008[8] and different ways are explored for H_2O_2 reduction and radical scavenging, using either redox ions/nanoparticles (reversible due to self-regeneration during FC operation) or sacrificial groups (non-reversible). To allow homogeneous distribution and immobilization of the stabilizing functions in the host ionomer membrane, the hybridization process by the introduction of a SG phase seems to be promising. Recently our team has shown that self-condensing SG precursors like (3-mercaptopropyl)trimethoxysilane (MPTMS) inside a pre-existing membrane (no solvent casting but impregnation of the host membrane) is an efficient way to physically and chemically stabilize sPEEK membranes which are prone to fast chemical oxidation and short lifetime in FC (500 hours vs. 50000 hours for Nafion membrane)[9,10]. Some other antioxidants functions of the organosulfide familiy's have been studied to find the most effective one against sPEEK chemical attack and mechanical preservation. Thiourea functions appear as the most promising[11].

In this present paper we focus on the strategy we used to determine the effectiveness of the stabilization provided by the functionalized SG phase after having exposed the membranes to a specific accelerated aging test.

2. Experiments

2.1 Hybrid membrane materials and fabrication process

The impregnations of sPEEK membranes were realized in the C2PM laboratory. The SG phase was grown by self-condensation of the SG precursor inside a commercial sPEEK host membrane.

The starting commercial sPEEK (sulfonated polyetheretherketone) membranes with an IEC of 1.34 meq.g^{-1} were purchased from Fumatech. The N,N'bis[3-triethoxysilyl)propyl]thiourea (Hexa-thiourea or HTU) precursor was purchased from Gelest.
Process of fabrication steps were detailed in previous publications[10,12] and is briefly presented hereafter.

Prior to impregnation, the host commercial sPEEK membranes were re-acidified (A) in a 1M HCl solution at room temperature for 4h, triple rinsed with pure water, hydrothermally treated in liquid water at 80°C for 72h to improve the nano-phase separation between hydrophilic and hydrophobic domains[13,14]. At this stage, the membrane is labelled sPEEK_NS (NS for NanoStructured). Then membranes were swollen for 24h at 30°C in an acidified (acetic acid addition down to pH 4) water/ethanol (HA) mixture (64/36 volume composition) to condition the membranes prior to SG impregnation.
SG precursors were pre-hydrolyzed (stirred for 2h at room temperature) into the same solvent mixture as the one used for membrane swelling to obtain a homogeneous solution. The host sPEEK membrane was immerged (I) into the previous SG solution during 25h at 30°C. After this impregnation step, the membranes were removed from the solution and dried in an oven under a nitrogen flux at room temperature overnight prior a post condensation (PC) step of 24h at 80°C under nitrogen. Finally, an additional hydrothermal post treatment (PT) step (in liquid water at 80°C for 72 h) was applied to elute uncondensed SG oligomer[15] and to improve its proton conductivity. Finally the membranes were re-acidified before FC operation.

2.2 Gravimetric measurements: SG and water uptake

The SG uptake (SGupt) of the hybrid membrane was calculated from gravimetric measurements of the mass of sPEEK_NS and mass of the hybrid membrane in the dry state (dried in an oven under a nitrogen flux at room temperature overnight).

$$SG_{Upt} = \frac{mHyM_{dry} - msPEEK\_NS_{dry}}{msPEEK\_NS_{dry}} \times 100\%$$

The hybrid membrane Water Uptake (W_{Upt}) in liquid water at 25°C was calculated as follows:

$$W_{Upt} = \frac{mHyM_{wet} - mHyM_{dry}}{mHyM_{dry}} \times 100\%$$

To measure the mass of the water-swollen hybrid membrane, $mHyM_{wet}$, excess water on surfaces was removed from the membrane using absorbent paper just before weighing.

2.3 Proton conductivity (σ)

The in-plane resistance was measured by voltamperometry, by performing a linear voltage sweep (LSV) using an Essential VSP Potentiostat (BioLogic Science Instrument) and a BT-110 conductivity clamp (four-electrode method[16] Scribner Inc.,USA) at room temperature and in hydrated state (at least 24h in liquid water), after equilibrium in water at 80°C during 72h and a re-acidification with 1M HCl solution during 4h at room temperature. The slope of voltage vs. current response was used as the resistance (R in Ω) in the in-plane conductivity, σ (S cm^{-1}), calculated according to:

$$\sigma = \frac{L}{W \times e \times R}$$

where L is the distance between the inner V-sense electrodes (cm), W is the membrane width (cm) and e is the membrane thickness (cm).

2.4 Durability test

2.4.a Accelerated ageing test

To evaluate the efficiency of the sacrificial functions of the SG phase to mitigate oxidative attacks, accelerated aging tests were performed in H_2O_2 solutions (prepared by mixing 30 wt% H_2O_2 solution with pure water, without ferrous additives to avoid ionic exchange with the membrane). H_2O_2 concentration from 0.1 to 1 wt% were tested and volumes of oxidizing solution were kept proportional to the mass of dry hybrid membrane (2ml/mg). The chemical attacks were thermally activated at 80°C for 24h.

2.4.b Quantification of the extent of degradation

The extent of degradation of the membrane was performed on Nicolet iS50 FT-IR (Thermo Scientific) by IR analysis (transmission) of the aged membranes (degradation products trapped in the membrane) and U-Visible analysis of the aging solution (eluted products) on NanoDrop 200c Spectrophotomer (Thermo Scientific). Physical observations corresponding to the water uptake of the membrane, and to the membrane's weight loss (after drying) were obtained by gravimetric measurements.

3. Results

In-plane conductivity measurement and W_{Upt} measurements were performed on HTU hybrid membrane (hexa-thiourea precursor) at different SG_{Upt}. As expected, results reported on figure 2 show that the increase of SG_{Upt} induces a strong decrease of the W_{Upt} and the conductivity. However, The W_{Upt} and the conductivity of a membrane with a SG_{Upt} of 7% remains acceptable to be used in PEMFC : W_{Upt} = 150% and σ = 50mS/cm for the hybrid membrane against 200% of W_{Upt} and 70mS/cm for sPEEK. In consequence, functional properties still high.

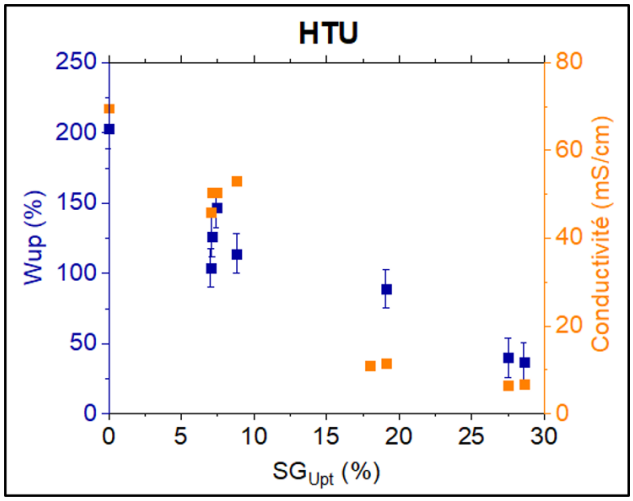


Figure 1: Evolution of the proton conductivity (orange) and the water uptake (blue) of hybrid HTU membranes versus the SG_{Upt}

HTU Hybrid membranes were exposed to H_2O_2 for evaluate the ability of the SG phase i.e. the thiourea function to inhibit the sPEEK phase degradation.

The water uptake and the weight loss of the aged samples according to the H2O2 concentration is reported on figure 3 for a sPEEK NS (reference material) and a HTU hybrid membrane with a SG uptake of 7%.
First, the water uptake and the loss of mass of the refernce material (sPEEK NS) increase quickly after a concentration of 0.4% in H_2O_2 in the solution. Conversely, the water uptake of the HTU hybrid membrane does not change significantly up to 0.9% H2O2 even if a slight loss of mass is observable from 0.1% H2O2. As expected, Weight loss decreases drastically with the addition of a larger amount of SG phase.

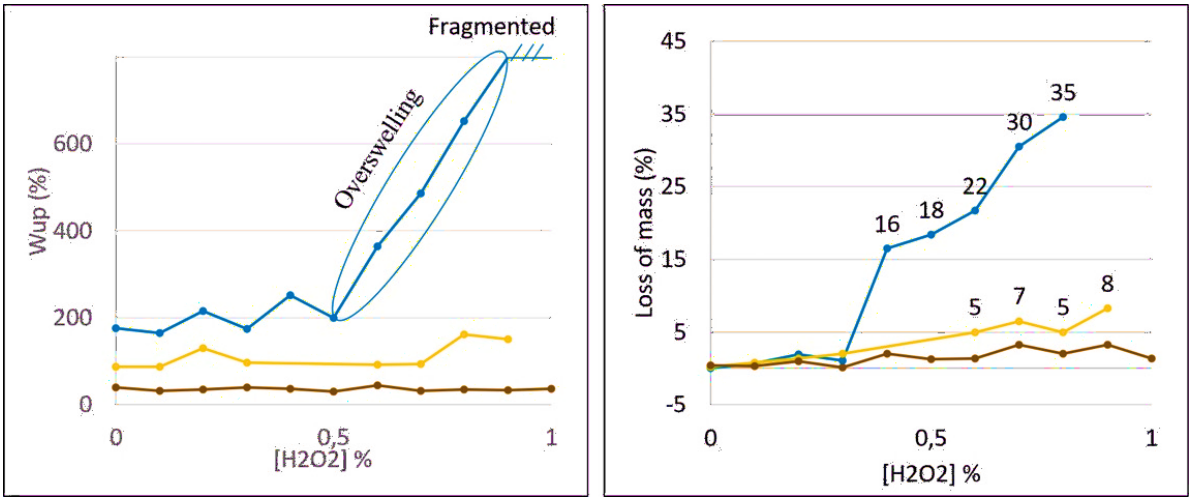


Figure 2: Evolution of water uptake (left) and loss of mass (right) of sPEEK_NS membrane (blue), HTU 6.5%SG (yellow) and 28.6%SG (brown) depending on the degrees of exposition to H_2O_2

A loss of mass at this stage indicates the elution of degradation products in H_2O_2 solution during the ageing test. In consequences, UV spectrum were acquired on these solutions. The results are reported on figure 4. The extent of degradation of the sPEEK phase of the hybrid membrane was measured by UV-Visible (UV absorption at 295 nm is characteristic of sPEEK degradation products found in the oxidizing solution after ageing tests). One can observe that a lower amount of sPEEK degradation products was released in the solution when increasing the SG_{Upt}.
To get a complete overview of the extent of membrane degradation, we next looked at the products trapped in the membrane. These products were quantified by IR (transmission) spectroscopy.
The literature and the FTIR spectra acquired on sPEEK membrane indicate that sPEEK degradation products have an absorption band at 1729cm^{-1}. For hybrid HTU membranes, for low concentration of H_2O_2 only an absorption band at 1700cm^{-1} is observed. This band is associated to the degradation of the SG phase and more precisely to the oxidation of the thiourea function and its hydrolysis to carbamic acid. The absence of degradation products characteristic of a sPEEK oxidation both in the membrane and in the aging bath demonstrates the protective effect of the SG phase.

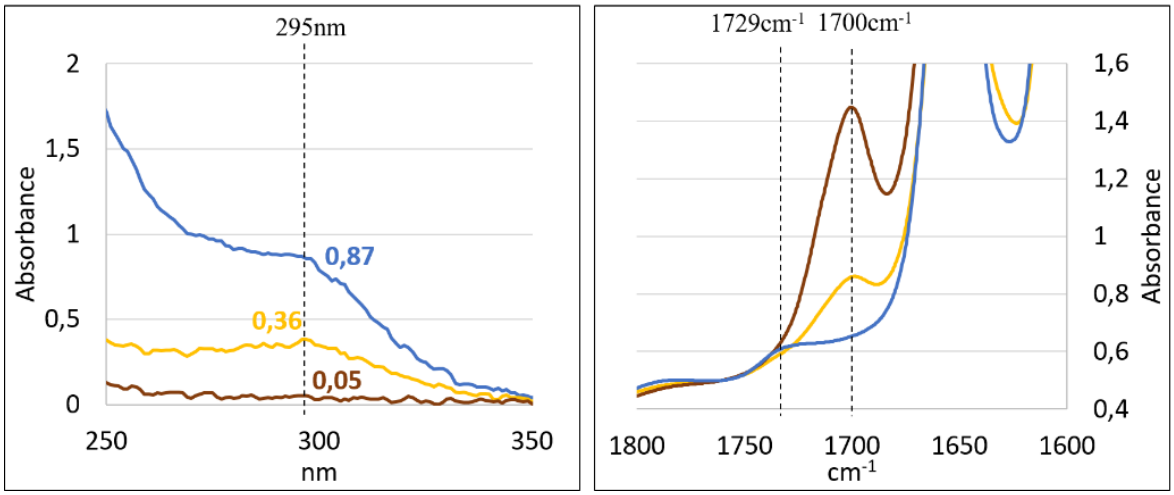


Figure 3: UV (left) and FTIR (right) spectrum of sPEEK_NS membrane (blue), HTU 6.5%SG (yellow) and 28.6%SG (brown) at respectively 0.7% and 0.2% of H_2O_2

The image obtain by TEM (Performed on JEOL JEM-3010) on figure 5 shown smalls spheres (about 5nm) well distributed in the sPEEK membrane. These spheres are attributed to the SG phase due to their the Silicium atoms which have a great contrast with the carbonate sPEEK membrane under electron exposition.

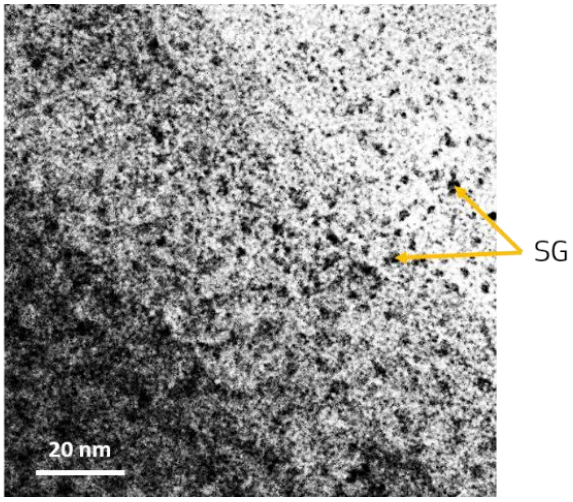


Figure 4: TEM image of hybrid HTU membrane with 28.6wt% of SG phase.

4. Conclusions

The present paper shows the results of the N,N'bis[3-triethoxysilyl)propyl]thiourea precursor to condensed into a host commercial sPEEK membrane and acts as a protection for the sPEEK phase. Our accelerated ageing test strategy demonstrates that stabilization of polyaromatics membranes very prone to oxidation can be tested without using ferrous ions. Our data process which combines physical observations with chemical analysis that are complementary, proved that the SG phase introduce by a HTU precursor is active and protects the sPEEK phase. Moreover, first characterization of morphology of the hybrid membrane shows that the HTU SG precursor seems to have condensed in spheres well dispersed into the host membrane.

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