Experimental report

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Title: SANS INVESTIGATION OF A NEW GENERATION OF HYBRID MEMBRANES FOR LONG-LIVED ELECTROLYZERS AND FUEL CELLS.

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: $C_{19}H_{12}O_3S$

Instrument	Requested days	Allocated days	From	To
D22	2	2	04/03/2021	05/03/2021
			25/06/2021	26/06/2021

Abstract:

We recently presented the elaboration of a new generation of hybrid membranes for PEMFC applications endowed with promising performances and durability, A chemically and physically active Sol-Gel (SG) phase was grown within a host membrane. Promising performances and durability were obtained. Combining AFM and SANS experiments we determined the structural features of the SG phase and the sPEEK nanostructure. To combine performance and durability, an in-depth study of the morphology of the membrane versus the chemistry of the SGPs is essential. This information can only be obtained by examining a large number of chemistry and formulation in order to have a predictive approach of the key parameters governing the final properties. We will vary (i) the SGPs chemistry/functionality/formulation and (ii) the SG phase content. This study will allow understanding the parameters controlling the SG localization and morphology. The results are expected to provide a comprehensive understanding of the structure/transport/durability/functional properties interplay, which is of fundamental interest to improve the design of efficient, durable and performing membranes.

SANS INVESTIGATION OF A NEW GENERATION OF HYBRID MEMBRANES FOR LONG-LIVED ELECTROLYZERS AND FUEL CELLS

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The aim of the present study was to investigate the morphology of a new generation of hybrid membranes for proton exchange membrane fuel cells (PEMFC), endowed with promising performances and durability. A chemically and physically active Sol-Gel (SG) phase was grown by self-condensation of hexafunctional and trifunctional thiourea (labelled HTU and TTU respectively) based SG precursors inside a commercial sPEEK host membrane to protect it against oxidizing agents generated during fuel cell operation. We observed that the SG phase makes it possible to **limit the impact of aging on the physical properties of the membrane** (limited polymer weight loss and water uptake after aging in hydrogen peroxide solutions). We have studied by **Contrast Variation SANS (CV-SANS)** hybrid membranes with ~10, 20 and 30% SG content to (i) determine the SG network structural features and in turn, ascertain its location with respect to the different phase of the host membrane (ii) determine the **reciprocal structural impact of both phases (matching of sPEEK or SG phases).**

<u>Preparation of samples</u>. The hybrid membranes are labelled: HTU-X% and TTU-X% with X% the SG uptake. Prior to SANS experiments, the hybrid membranes were equilibrated in H_2O, D_2O or a mixture of both for at least 24 h, in order to vary the contrast between the polymer phase, the SG phase and the solvent.

<u>Main results</u>. In the case of HTU membranes, water uptake and conductivity decrease linearly with an increase of the SG uptake while for TTU membranes, there is no significant change in water uptake and conductivity with the SG uptake (up to a SG uptake of 30%). While both HTU and TTU protect sPEEK, we observed for the aging reactions an induction period (during which the material retains its initial properties) which decreases when TTU content increases.
These observations indicate that in addition to the chemistry, the SG/sPEEK physico-chemical interactions, the morphology and presumably the localization of the SG phase drive the functional properties of the hybrid membranes. In order to understand the structure-proprieties-durability function interplay, we explored the morphology of the hybrid membranes using a combination of direct space (AFM/SEM) and reciprocal space (SANS/WAXS) techniques (dimensional scale covered: from a hundred to a few manometers).

**** Matching the SG phase signal (SG phase extinction) => sPEEK phase observation***

(a) HTU ($\rho_{SG\_calc} \approx 1.26 \times 10^{10}/cm^2$ => 18 % D_2O) **(b) TTU ($\rho_{SG\_calc} \approx 1.74 \times 10^{10}/cm^2$ => 25 % D_2O)**

Fig.1. *SANS profiles of hybrid membranes under SG phase signal matching (sPEEK phase observation)*
(a) *HTU and* ***(b)*** *TTU for various SG uptake*

We observed that despite SG insertion, the ionomer peak, which is the fingerprint of the hydrophilic/hydrophobic nanophase segregation is observed, proving that the sPEEK ionic pathways are preserved (**Fig. 1a,b**). Noticeable rightward shift and widening of the ionomer peak are observed when increasing the SG content, which suggest **ion channel compression** (very slight for TTU membranes**)** and greater heterogeneity of the ionic domains respectively.

**** Matching the sPEEK phase signal (sPEEK phase extinction) => SG phase observation***

HTU. **Dry conditions: sPEEK/HTU phase contrast*. The small angle bump is attributed to the scattering of dispersed and polydisperse SG spheres (inset of **Fig. 2b**) compatible with TEM observations (**Fig. 2a)**. The spheres size determined by both techniques is in the ~5 nm range, whatever the SG uptake. These objects **are too large to be compatible with the dimensions of the ionic pathways of sPEEK** (~3 nm). The intensity of this bump increases without significant peak shifting which suggests that the number of SG sphere increases with SG content without pronounced sphere growth. A wider-angle correlation peak (Q~0.1 $Å^{-1}$) is observed in the same scattering range as the so-called ionomer peak (here sPEEK contrast matching conditions, *i.e* ≠ ionomer peak) and therefore represents scattering from SG domains created **in the sPEEK ionic domains** during the SG synthesis (called thereafter hybrid peak).

** Wet conditions: SG phase structure*. The origin of the flattening of the overall SANS profile under wet condition can be tentatively explained by a superimposition of the small angle signal with the hybrid peak that shifts towards small angles because of the ionic domains swelling.

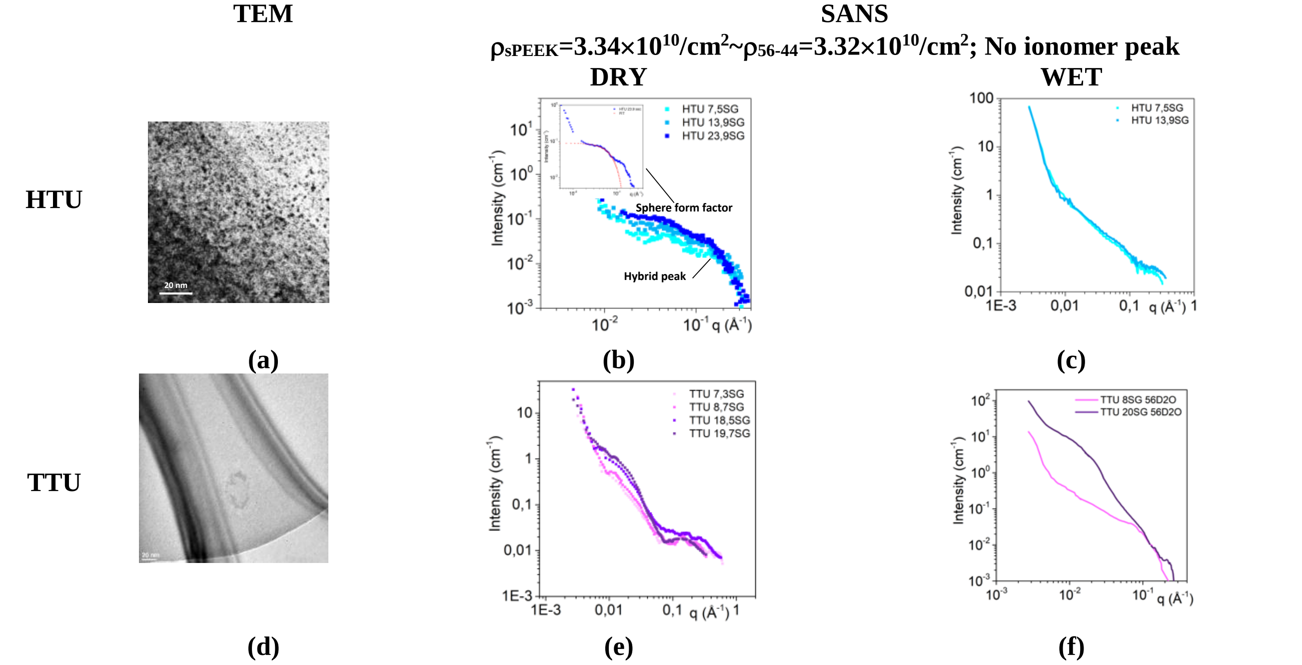

Fig. 2. ***TEM images** of HTU 28%* ***(a)*** *and TTU 18%* ***(d). SANS profiles** of hybrid membranes: HTU membranes in dry conditions (b) and under sPEEK matching conditions (c); TTU membranes in dry conditions (e) and under sPEEK matching conditions (f).*

TTU. **Dry conditions: sPEEK/HTU phase contrast.* A hybrid peak is also observed which shows that the ionic pathways of sPEEK were used as template of the growth of the SG phase. At smaller angle, a pronounced bump was measured while no objects were observed with TEM (no electronic contrast was observed between TTU and sPEEK) (**Fig.2d**). These contrasting observations illustrate the fact that TTU and sPEEK phase are intimately mixed at the nanometer length scale. In other words, part of the SG phase grows in the interbundle regions in close interaction with sPEEK amorphous chains. This organisation can generate a density fluctuation (inside/outside the bundles) at the origin of the small angle SANS signal and a poor electron contrast (no signal).

** Wet conditions: SG phase structure.* The hybrid peak is leftward shifted (swelling of the ionic domains). With respect to dry conditions, for TTU 8%, the small angle bump decreases in intensity with a noticeable rightward shift (SG domains get closer) while for TTU 20% the intensity increases and is accompanied with a leftward shifting (SG domains move away from each other). These observations can be explained by a phase inversion, *i.e.*, for low SG content, the interbundle regions can be described as SG phase inside sPEEK phase while for large SG content this is more likely sPEEK phase inside SG phase.

Conclusions. To combine performance and durability, this goes without saying that a precise study of the structure/properties/durability relationship is mandatory. To do so, an in-depth study of the morphology of the membrane with regard to the **chemistry** of the SG Precursors (stabilization group, number of hydrolyzable functions) is essential[1]. This information can only be obtained by examining a large number of chemistry and formulation in order to have a **predictive approach** of the **key parameters governing the final properties**.[2] Therefore, we need other SANS campaigns to target this goal.

References [1] N. Huynh, *et al J. Power Sources* **2020**, 462, 228164. [2] N. Huynh, et al *Nanoscale Advances* **2021** 3, 2567-2576