



## Small-angle X-ray and neutron scattering study of Nafion-SiO<sub>2</sub> hybrid membranes prepared in different solvent media



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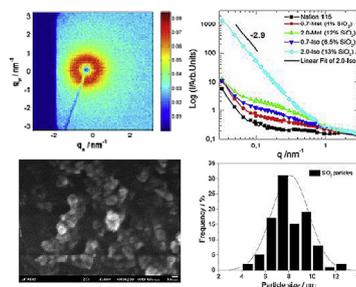
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### HIGHLIGHTS

- PFSA(Nafion)-silica hybrid electrolytes were synthesized by sol–gel route.
- The homogeneity and structural features of the nanocomposites were studied SEM/EDX, SAXS and SANS.
- The results indicate that the pristine PFSA structural may be preserved on the nanoscale.
- The proton conductivity of PFSA may be further improved by a moderate and careful incorporation of the silica phase.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Nafion-SiO<sub>2</sub> hybrid electrolytes were synthesized by sol–gel reaction. The homogeneity, structural properties, and proton conductivity of the hybrid membranes were studied. Small-angle scattering analyses indicate that the Nafion structural matrix was preserved on the nanoscale, and the growth of silica particles occurred both in the ionic and nonionic domains of Nafion, which resulted in hybrids with characteristic morphologies. The water uptake and the weight fraction of the inorganic phase were found to be dependent on the alcohol solvent used for the sol–gel synthesis. Nafion-silica hybrids with homogeneous distribution of the inorganic phase were obtained using methanol as the solvent for the sol–gel reaction. The observed microstructural properties of the Nafion-silica membranes were related to enhanced proton conductivity at high temperatures and low relative humidity conditions.

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## 1. Introduction

The use of electrochemical cells is a key concept in the decentralized generation of sustainable electricity. Batteries, capacitors,

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electrolyzers, and fuel cells are modular and complementary devices for electrochemical energy storage and conversion [1,2]. Notably, the polymer electrolyte fuel cell (PEFC) is particularly attractive for applications with variable electric load and intermittent operation, such as portable electronics, distributed power sources, and electric vehicles. Furthermore, there is the possibility of such devices to operate with diverse fuels such as hydrogen, methanol, and ethanol [2,3]. For operating temperatures below 100 °C, the perfluorosulfonic acid (PFSA) polymer electrolyte, usually DuPont's Nafion, is still the commercial benchmark and the standard material found in fuel cell assemblies. Such a polymer electrolyte at fully hydrated conditions can provide a favorable combination of proton conductivity and membrane chemical stability [1,2].

However, the fuel cell operation at higher temperatures and lower humidity levels has positive outcomes: the efficiency of the electrochemical catalysis is improved and problems related to water management inside the cell assembly are mitigated [4,5]. Additionally, if external humidifiers can be omitted, the weight and volume of the system can be reduced [6,7]. However, pristine PFSA are not suitable for such operating conditions, since increasing the temperature and decreasing the level of hydration result in severe loss of ionic conductivity. In this context, in order to obtain high energy conversion efficiency the PEFC electrolyte must attend several requirements such as high thermomechanical stability in the presence of different fuels (H<sub>2</sub>, ethanol, methanol) and high proton conductivity.

Several approaches have been proposed to prevent the conductivity loss of Nafion at low relative humidity and high temperature (at constant water partial pressure) [1–4,6]. A straightforward approach is the addition of a hygroscopic phase within the PFSA matrix, and thus, forming a hybrid nanocomposite [8,9]. Usually, inorganic oxides are employed for forming the hygroscopic phase [1,8]. In order to promote specific changes in the electrical properties of Nafion, ideally, a strong coupling between the PFSA's ion-rich domains and the hygroscopic phase must be achieved, and the inorganic phase also acts as a structural reinforcement for the electrolyte matrix [9].

Nafion-oxide membranes have been produced mainly by two distinct routes: i) by dispersion oxide particles, such as SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, in Nafion solution with subsequent formation of the film by recasting, referred to as “composite membranes” and ii) by *in situ* sol–gel synthesis, where the inorganic particles are synthesized by sol–gel reactions inside of the commercial Nafion membranes. Such membranes are referred to as “hybrid membranes”. Considerably different properties are observed due to the distinct fabrication methodologies [8].

Although a considerable interest and effort have been dedicated to Nafion-based hybrid membranes [10–12], the influence of the inorganic phase on the nano-phase segregated structure of the PFSA is not fully understood [13]. Important features, such as the location of the inorganic phase inside the PFSA matrix, are expected to be crucial for mass transport and ionic conductivity in Nafion-silica hybrids. Nevertheless, only a few studies have investigated the relation between the microstructure and electrical properties of Nafion-silica hybrids [9,11,15,16].

In our previous work [16], the effect of the alcohol type employed in sol–gel Nafion-SiO<sub>2</sub> synthesis was investigated. The results showed that the alcohol controls the silica particle distribution into the Nafion structure and strongly influences the properties of hybrid membranes. In the present study the impact of both solvent and silica fraction on the nanostructure of Nafion-silica hybrids were further evaluated by detailed small-angle scattering techniques (SAXS, SANS) and transport measurements.

## 2. Experimental

The Nafion-silica hybrid membranes were prepared by following the same procedure reported previously [16]. Nafion-silica hybrids were synthesized by using commercial Nafion 115 membranes (H<sup>+</sup>, 127 μm thickness, DuPont) as the matrix for the *in situ* incorporation of silicon dioxide via sol–gel. Prior to the sol–gel synthesis, the membranes were treated in a hydrogen peroxide solution (3% v/v) at 80 °C for 1 h to eliminate the organic impurities. This step was followed by successive water baths at the same conditions to remove any H<sub>2</sub>O<sub>2</sub> trace. Membranes were swollen in sulfuric acid 0.5 mol L<sup>-1</sup> at 80 °C for 1 h to ensure that the polymer is in the acid form, and then they were washed in water in the same conditions to eliminate the acid residues. Finally, membranes were dried at 105 °C for 24 h in a vacuum oven.

The sol–gel synthesis began with swelling Nafion in alcoholic solvent for 0.5 h in a closed vessel [14]. Three alcohols were used as solvent for swelling the pristine membrane: methanol (Met), ethanol (Et), and isopropanol (Iso). The use of different kind of alcohols was motivated by previous studies reporting that each solvent results in different swelling of PFSA membranes [12,14], and consequently, different interactions between the solvent and the polymeric matrix is expected, e.g. different absorption levels, which may influence the structural and electrochemical properties of hybrid membranes [12,14]. Subsequently, the silica precursor TEOS (tetraethyl orthosilicate, Aldrich) was added with concentrations of 0.7 and 2.0 mol L<sup>-1</sup>, respectively, and kept for 0.5 h.

The hydrolysis reaction of TEOS was carried out by acid catalysis using nitric acid (0.5 mol L<sup>-1</sup>) at 50 °C for 0.5 h. The membranes were removed from the reaction medium and the condensation reaction was promoted in a vacuum oven at 95 °C for 24 h. Finally, the resulting membranes were treated with H<sub>2</sub>SO<sub>4</sub> 0.5 mol L<sup>-1</sup> and water at 80 °C to remove residues and unstable particulate remnants. The hybrid nomenclature was defined in function of TEOS concentration and solvent used in sol–gel media.

The silica incorporation degree in hybrids Nafion-silica was defined as:  $\Delta_{\text{SiO}_2} (\%) = (m_N - m_H) / m_N$ , whereas  $m_N$  the unmodified Nafion mass and  $m_H$  the mass of the hybrid membrane after incorporation of the silica. Water uptake of pristine Nafion and hybrids was defined as:  $\Delta m (\%) = (m_S - m_D) / m_D$ , whereas  $m_S$  the water saturated membrane mass and  $m_D$  the mass of the dry membrane. Dry membrane ( $m_D$ ) was evaluated by weighting the samples after thermal treatment at 110 °C for 24 h in vacuum. Water saturated membrane mass ( $m_S$ ) was determined after immersed in water at room temperature for 1 h and the excess of water on the membrane surfaces was removed by using a qualitative filter paper before weighting.

The morphology of the hybrids was studied by field-emission scanning electron microscopy (FE-SEM, JEOL model JSM-6701F) and the chemical characterization was conducted by using energy-dispersive X-ray spectrometer attached (EDX, Thermo Scientific, model NORAN System – Nano Trace detector). The thin/sliced samples used in SEM/EDX analysis were obtained by cutting the membranes with a diamond-coated blade. It was possible to obtain images with high magnification using a low acceleration voltage (5 kV) without sample degradation, confirming the presence of SiO<sub>2</sub> nanoparticle agglomerates. Besides the low electrical conductivity of Nafion, samples were not coated to avoid possible misinterpretations.

Small-angle X-ray scattering (SAXS) spectra of dry membranes (pristine Nafion, 2.0-Met, 2.0-Et, 2.0-Iso) were recorded with S-MAX3000 pinhole camera operating with  $\lambda = 0.1524$  nm of photon wavelength (Rigaku Innovative Technologies, Auburn Hills, USA). SAXS spectra were recorded in acid (SO<sub>3</sub><sup>-</sup>H<sup>+</sup>) as well as Cs-salt form

( $\text{SO}_3^- \text{Cs}^+$ ) in order to enhance the scattering contrast for the ion-rich aggregates. For converting the membranes into the Cs-salt form, membranes were immersed in 0.5 M CsCl solution at room temperature for 10 h to ensure the complete exchange of  $\text{H}^+$  by  $\text{Cs}^+$ . After ion exchange, the membranes were carefully rinsed with water and dried at 50 °C under vacuum. The dry membranes were not hydrated prior to the measurement and were kept in vacuum at room temperature during the measurements.

Small-angle neutron scattering (SANS) experiments were performed at dry and saturated environments at the Swiss Spallation Neutron Source SINQ, using the SANS-II beamline, Paul Scherrer Institut, Villigen, Switzerland. Measurements were carried out using three different scattering geometry settings: sample-to-detector distance of 1.2, 3, and 6 m with neutron wavelengths of 0.45, 0.7 and 1.04 nm, respectively. The fully hydrated membranes were kept in a sealed quartz cell at ambient temperature. For SANS contrast variation study, five different mixtures of normal and deuterated water were used, where  $\text{H}_2\text{O}-\text{D}_2\text{O}$  vol.% – vol.% is equal to a.) 0–100, b.) 24–76, c.) 40–60, d.) 76–24, e.) 100–0.

Raw SAXS/SANS data were processed according to standard procedures [17]. All scattering spectra were isotropic, and therefore, the scattering spectra were presented as a function of the scattering vector modulus  $q = 4\pi \cdot \lambda^{-1} \cdot \sin(\theta/2)$ , where  $\theta$  is the scattering angle and  $\lambda$  (nm) is the neutron/photon wavelength.

Proton conductivity of pristine Nafion and hybrids Nafion-SiO<sub>2</sub> was measured by electrochemical impedance spectroscopy (EIS) performed in through-plane direction by using a Solartron 1260 Impedance/Gain Phase Analyzer in the frequency range of 1 Hz–1 MHz and 100 mV ac amplitude. EIS measurements were performed in 40–130 °C temperature range with 100% relative humidity (RH) and at 130 °C as a function of RH. In order to have a simultaneous control over the relative humidity and temperature, an airtight sample holder was used [18]. The sample holder has spring-load contacts, electrically insulated from the body of the apparatus. A constant pressure is maintained during the conductivity (through-plane) measurements. Further details of both the sample-holder and of the conductivity measurements are provided elsewhere [18]. Briefly, conductivity measurements were performed upon heating by following a strict protocol to allow both temperature and relative humidity equilibration. For measurements at constant RH = 100%, the wet samples was positioned in the sample holder and the EIS data were collected after 30 min of stabilization at each measuring temperature. For measurements at varying RH, samples were firstly dried in a resistive oven under continuous air flow, positioned in the sample holder, and exposed to increasing RH values at fixed temperature (130 °C). For each measuring RH, EIS data were collected after 30 min of stabilization. The RH of the sample chamber was calculated by:  $RH = \rho(T_r)/$

$P(T_c) \times 100$ , whereas  $\rho$  is the saturated vapor partial pressure,  $P$  is the vapor partial pressure, and  $T_r$  and  $T_c$  are, respectively, the water reservoir and sample chamber temperatures.

### 3. Results and discussion

Table 1 shows the weight fraction of silica incorporated and the water uptake values for pristine Nafion and Nafion-SiO<sub>2</sub> hybrids prepared with different TEOS concentration and sol–gel solvent.

Incorporation of silica is found to be dependent on the TEOS concentration and on the nature of alcohols employed in the sol–gel synthesis, in accordance with previous reports [16,19]. The weight fraction of silica can be associated with the solvent uptake of unmodified Nafion, which can facilitate the absorption of the silicon precursor (TEOS), and consequently the growth of the silica network [16,19]. The sol–gel silicon dioxide phase in Nafion films was shown to consist of a fractal-like growth of the inorganic phase, which establishes interconnections with increasing volume fraction inside the matrix [19]. Another factor influencing the incorporation of silica can be linked to the distinct interactions between the given solvent and the ionomer matrix [20]. The different degree of swelling of Nafion with the solvents can promote the hydrolysis and condensation of silica into different domains of the ionomer nanostructure [16,19]. Based on previous SANS studies, the swelling of Nafion membranes with methanol occurs preferentially in the ionic phase of Nafion, while the ionic phase is much less sensitive to the ethanol and propanol uptake [20]. Such characteristics indicate that ethanol/propanol molecules can be solvating both ionic and nonionic domains of Nafion [20] and can possibly affect the degree of silicon oxide incorporation.

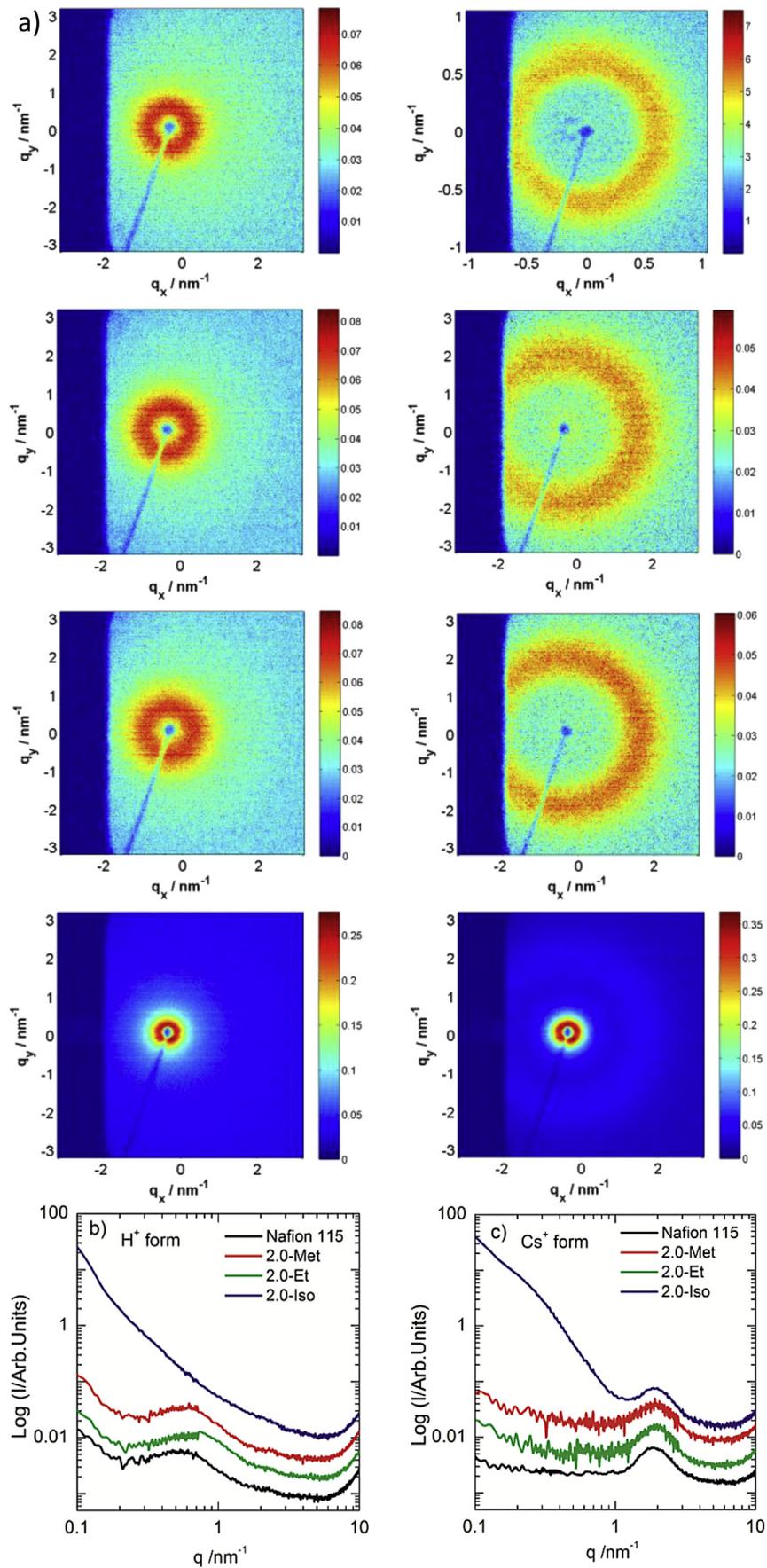
Nafion-SiO<sub>2</sub> hybrid membranes present superior water uptake in comparison with unmodified Nafion. It is a rather general trend that the Nafion-SiO<sub>2</sub> hybrids prepared with both ethanol and isopropanol display higher water uptake. However, there is no systematic relation between the silica content and the water uptake. The higher water uptake of the hybrids prepared in ethanol/isopropanol solvents can result from the water absorption at the silicon dioxide surface. The water uptake of ionomers is dependent on the equilibrium between the electrostatic forces among solvated charges, the osmotic pressure of the counterions, and the elastic deformation of the polymer chains [21]. The nearly constant water uptake for different silica concentrations indicates that the absorption of higher amounts of water is inhibited by the elastic forces of the polymer chains. Electrolytes with high water uptake are desirable for a better conductivity, since a higher amount of water can promote structural proton diffusion with respect to the vehicular mechanism [22].

Fig. 1 shows SAXS spectra of dry samples of Nafion and Nafion-SiO<sub>2</sub> hybrids in  $\text{H}^+$  and  $\text{Cs}^+$  forms. The two-dimensional SAXS patterns (Fig. 1a) are isotropic, indicating that the dispersion and orientation of heterogeneities within the polymer is isotropic. It has been previously reported that the SAXS patterns of dry Nafion membranes display two characteristic scattering maxima centered at  $q \sim 2 \text{ nm}^{-1}$  and  $q \sim 0.7 \text{ nm}^{-1}$ , which are mainly attributed to the correlation length between Nafion polymeric aggregates (ionomer peak) and to the interlamellar distance between Teflon-like crystallites (matrix peak) [21], respectively.

In the acid form, apart from the 2.0-Iso sample, the matrix peak dominates the scattering spectra (Fig. 1b), and the ionomer peak is not evident. This is due to the low contrast between the ionic and non-ionic phases in the dry samples. The position and shape of the matrix peak remain essentially unaltered upon the incorporation of silica, using methanol and ethanol solvents. These solvents probably result in a lower interconnectivity between silica particles or a better dispersion of the inorganic phase in the Nafion matrix. The

**Table 1**  
Silicon precursor concentrations used for different sol–gel solvents, silica weight fraction, and water uptake of the hybrid electrolytes.

Sample	TEOS [mol L <sup>-1</sup> ]	SiO <sub>2</sub> [wt.%]	Water uptake (%)
Nafion 115	–	–	30
0.7-Met	0.7	4	38
1.0-Met	1.0	4.5	39
1.5-Met	1.5	10	34
2.0-Met	2.0	12	38
0.7-Et	0.7	3	45
1.0-Et	1.0	6	48
1.5-Et	1.5	12	42
2.0-Et	2.0	13	43
0.7-Iso	0.7	6.5	38
1.0-Iso	1.0	7.4	47
1.5-Iso	1.5	11	43
2.0-Iso	2.0	13	41



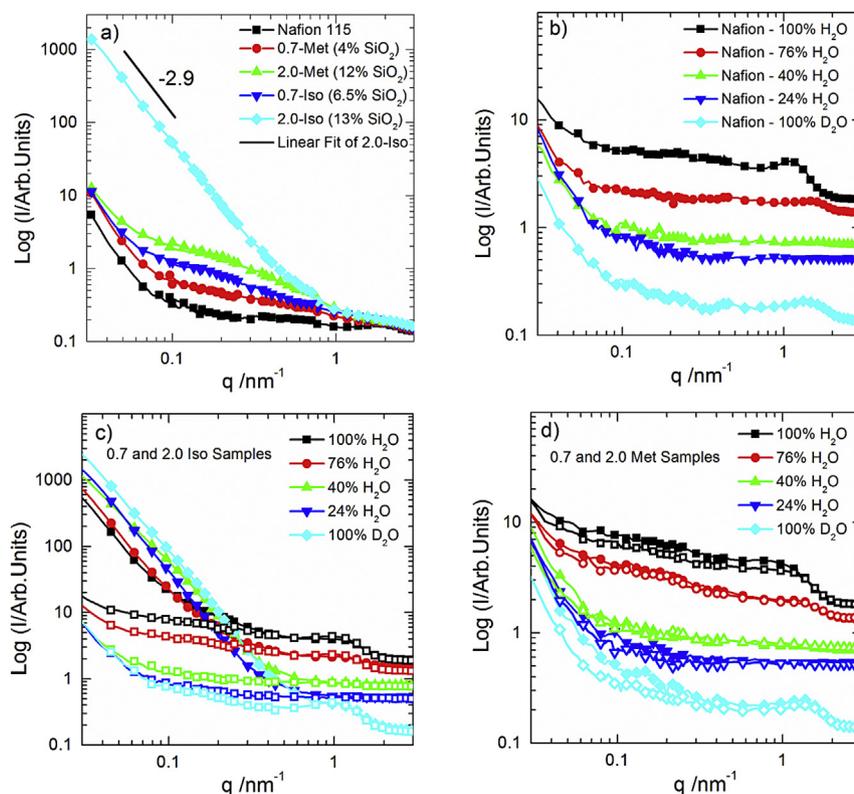
**Fig. 1.** SAXS spectra of dry samples of Nafion and Nafion-SiO<sub>2</sub> hybrids: (a) 2D scattering patterns of Nafion and Nafion-SiO<sub>2</sub> hybrids in H<sup>+</sup> (left) and Cs<sup>+</sup> forms (right). Samples are Nafion, 2.0-Met, 2.0-Et, and 2.0-Iso (from top to bottom). For the case of 2.0-Iso, the strong scattering at low  $q$  values completely dominate the scattering pattern. (b) Azimuthally averaged spectra from the electrolytes in the acid-form, and (c) spectra from the electrolytes in the Cs-salt form.

contrast between the polymer matrix and the inorganic phase is not high, and the overall volume of the inorganic phase is moderate (i.e. max. 13 wt. %). This can explain why the polymer heterogeneities, found already for Nafion, dominate the SAXS spectra of the hybrids. On the other hand, the scattering spectrum of the Nafion SiO<sub>2</sub> prepared in isopropanol displays a strong upturn in intensity. A similar trend of scattering intensity has been observed for polymer-oxide composites, and is associated with the agglomeration of inorganic nanoparticles [23]. This view is also supported by previous infrared and NMR studies of sol–gel prepared Nafion-SiO<sub>2</sub> that showed increased connectivity of the silica network at high inorganic weight fractions [14].

Fig. 1c shows the SAXS pattern of cesium-neutralized samples. Contrary to the protonated hybrids (Fig. 1b), the ionomer peak for the samples in the Cs<sup>+</sup> form is well-defined owing to the increased contrast between ionic and non-ionic domains. In agreement with the increased contrast for the ionic domains, the matrix peak is not observed in Cs<sup>+</sup> samples, similarly to previous reports [24]. The ionomer peak position is not affected by the presence of the inorganic phase, similarly to the matrix peak shown in Fig. 1b. A rough estimate of the full width at half height of the ionomer peak for Nafion (~1.4 nm<sup>-1</sup>), Nafion-SiO<sub>2</sub>/Et (~1.4 nm<sup>-1</sup>), and Nafion-SiO<sub>2</sub>/Met (~1.8 nm<sup>-1</sup>) revealed a broader peak for the hybrid prepared in methanol solution. This can be associated to an increased heterogeneity of the ionomer domains promoted by the silica addition. As the ionomer peak position is related to the characteristic distance between ion-rich aggregates, it is likely that the silica network in hybrids prepared in methanol solution changes the distribution of such ionic domains. This result is in good agreement with previous SANS studies of Nafion in different solvents that indicated that the ionomer peak position and shape are strongly dependent on the

methanol uptake [20]. The preferential swelling of the Nafion's ionic domains in methanol can promote a more localized synthesis/nucleation of silica particles in the interior of the ionic clusters; however, the incorporation of silica has not affected significantly the ionomer peak. This finding indicates that the ion-rich aggregates of Nafion are preserved, and suggests that the inorganic phase may permeate both ionic and nonionic domains of the ionomer matrix. Similarly to the spectrum recorded in the H<sup>+</sup> form, the spectrum of the Nafion-SiO<sub>2</sub>/Iso in the Cs<sup>+</sup> form reveals an intensity upturn for lower  $q$ . Such low  $q$  scattering can relate to large silica domains, e.g. formed by aggregation, with a fractal-like structure of the inorganic phase [23]. Therefore, SAXS data strongly suggest that the interactions of the different solvents with the ionomer matrix can result in the incorporation of silicon dioxide in distinct domains of Nafion's phase-segregated structure. The role of the solvents in the distribution and localization of the nanoparticles is then further studied by SANS contrast variation measurements (Fig. 2).

In some SANS patterns the ionomer and matrix peaks are not clearly identified. This is probably associated with the moderate scattering contrast between the ionic and non-ionic phases. The SANS patterns of dry Nafion-SiO<sub>2</sub> prepared in methanol solutions (Fig. 2a) are very similar to the ones observed by SAXS (Fig. 1), the ionomer and matrix peaks are essentially unaltered with respect to Nafion scattering pattern indicating that the matrix is preserved after the incorporation of the inorganic phase. The overall increase in the scattered intensity, compared to Nafion, reflects on the higher neutron scattering contrast between the silica and PTFE, in relation to the smaller contrast between amorphous and crystalline PTFE as well as between the ionic and non-ionic phases. The extended scattering range of SANS further demonstrates the dominant low- $q$  intensity for the 2.0-Iso hybrid sample. For



**Fig. 2.** (a) SANS spectra of Nafion and hybrids membranes at dry state; (b) SANS contrast variation spectra of pristine Nafion in acid-form; SANS contrast variation spectra of Nafion-silica hybrids synthesized using (c) isopropanol and (d) methanol. The open symbols in (c) and (d) correspond to the 0.7-Met/Iso and the filled symbols correspond to the 2.0-Met/Iso hybrids, respectively.

$q < 0.4 \text{ nm}^{-1}$  the SANS curve of the isopropanol hybrid follows a  $-2.9$  power law (Fig. 2a) that suggests the presence of highly heterogeneous silica domains with fractal properties [26,27]. On the other hand, the absence of the scattering upturn at low  $q$  for the hybrids prepared in ethanol and methanol is again an indication of the high degree of dispersion of the inorganic phase in the ionomer matrix achieved for these solvents.

In Fig. 2b, it is interesting to note that the ionomer peak is suppressed at intermediate  $\text{H}_2\text{O}:\text{D}_2\text{O}$  ratios, whereas for fully deuterated and protonated water the ionomer peak is evident. Previous reports showed that with increasing fraction of deuterated water the relative intensity of the ionomer peak decreases [21]. The effect of deuterated water on SANS curves of Nafion membrane and hybrids is difficult to predict due to the presence of the ionomer and matrix peaks [21]. Previous reports showed that the shape and the position of the scattering curves in SANS patterns of highly swollen Nafion (16 wt.% of polymer phase) changed with increasing  $\text{D}_2\text{O}:\text{H}_2\text{O}$  ratio [21]. Such finding relates the origin of the Nafion SANS pattern to the contrast between the polymer aggregates with a condensed layer of counterions and the solvent [21]. In this scenario, the presence of mixed amounts of protonated and deuterated water may change the distribution of condensed counterions and decreases the correlation existing between the polymer and the counterions, eventually suppressing the ionomer peak [21,25].

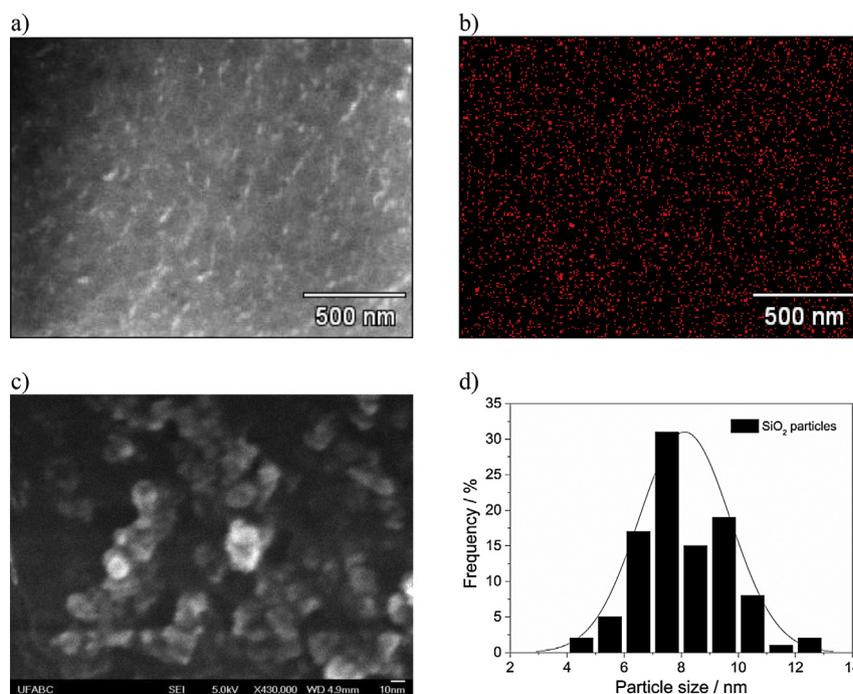
Upon absorbing water, the electrolytes swell and the ionomer peak shifts to lower  $q$ -values, as shown in Fig. 2c [21]. The ionomer peak for the composite electrolytes is broader than that of the pristine Nafion. The ionomer peak broadening can be a result of a less localized water sorption, compared to Nafion, due to possible presence of a hydrophilic silica phase in the nonionic domains. This, on the one hand can decrease the contrast between the polymer and the aqueous phase, and on the other hand can increase further the distance between hydrated ionic domains. SANS, therefore, suggests a higher level of distribution and connectivity of the hydrophilic phase, compared to Nafion. SANS contrast variation also

reveals that each electrolyte, again similarly to Nafion's original structure, has a structure more complex than a pure biphasic system, since by varying the scattering contrast set the ratio of the deuterated- and normal water in the mixture, both the amplitude and the features of scattering curve exhibit dependence.

As a final remark, it is interesting to note that scattering related to the ionomer peak is 'suppressed' at intermediate  $\text{H}_2\text{O}:\text{D}_2\text{O}$  ratios, whereas for fully deuterated and protonated water the ionomer peak is evident. It was shown that with increasing fraction of deuterated water the relative intensity of the ionomer peak decreases [21]. The effect of deuterated water on SANS curves of Nafion membrane and hybrids is difficult to predict due to the presence of the ionomer and matrix peaks [21]. Previous reports showed that the shape and the position of the scattering curves in SANS patterns of highly swollen Nafion (approximately 16 wt.% of polymer phase) changed with increasing  $\text{D}_2\text{O}:\text{H}_2\text{O}$  ratio [21]. Such finding relates the origin of the Nafion SANS pattern to the contrast between the polymer aggregates with a condensed layer of counterions and the solvent [21]. In this scenario, the presence of mixed amounts of protonated and deuterated water may change the distribution of condensed counterions and decreases the correlation existing between the polymer and the counterions, eventually suppressing the ionomer peak [21,25].

In summary, SANS also suggests an improved distribution of the inorganic phase (and thus, of the aqueous phase as well) for the hybrids prepared in ethanol and methanol and a higher degree of agglomeration for the isopropanol-hybrids. This is in agreement with the SAXS analysis, and confirms that the alcohol-dependent swelling properties of Nafion [20] may affect the size and distribution of the nanoparticles.

Fig. 3 presents FE-SEM analysis of the surface of the 0.7-Met hybrid membrane. The hybrid membranes prepared in methanol exhibited higher thermal stability that allowed for performing FE-SEM analysis [16]. In the low magnification FE-SEM image of the bulk of the Nafion-silica sample (Fig. 3a), small particles/agglomerates are observed.



**Fig. 3.** FE/SEM analyses of a sliced surface of the hybrid electrolyte 0.7-Met: (a) FE-SEM image; (b) the respective EDX silicon mapping; (c) higher-magnification FE-SEM image; (d) particle size distribution estimated from FE-SEM images.

The corresponding silicon EDX mapping (Fig. 3b) confirms a homogeneous distribution of the inorganic phase in the sample. Silica particle size histogram (Fig. 3d) was obtained by counting ~100 particles in a selected area of the micrograph (Fig. 3c) using Gaussian-type fitting. The estimated particle sizes of sol–gel silica inserted into the Nafion polymeric matrix range from 4 to 13 nm, with a mean diameter of  $8 \pm 4$  nm. Considering that the ionic clusters have an average size of 5 nm [21,22], the distribution of particles sizes (Fig. 3d) again indicates that a fraction of the inorganic phase may exist within the ionic domains of Nafion as well as in the non-ionic regions of the ionomer matrix, in accordance with the SAXS/SANS analysis. However, the presence of silica particles larger than the hydrated ionic domains can be a result of the sol–gel synthesis of silicon dioxide in alcohol-swollen Nafion membranes.

These relatively large hydrophilic domains can improve the structural features relevant to the transport properties of the hybrid electrolytes (Figs. 4 and 5).

The temperature dependence of the electrical conductivity for Nafion and Nafion-silica hybrids is shown in Fig. 4. The electrical conductivity exhibits two well-defined temperature regions (I and II). Region I, below  $T = 90$  °C shows a typical thermally activated Arrhenius-type  $\sigma(T)$  process, whereas in region II ( $T > 90$  °C) an upturn of the proton conductivity is observed. Recent studies have concentrated on measuring the proton conductivity of Nafion and Nafion-based composites at high temperatures, both at constant relative humidity and constant water partial pressure [18,28–30]. Reported results indicated that at constant relative humidity

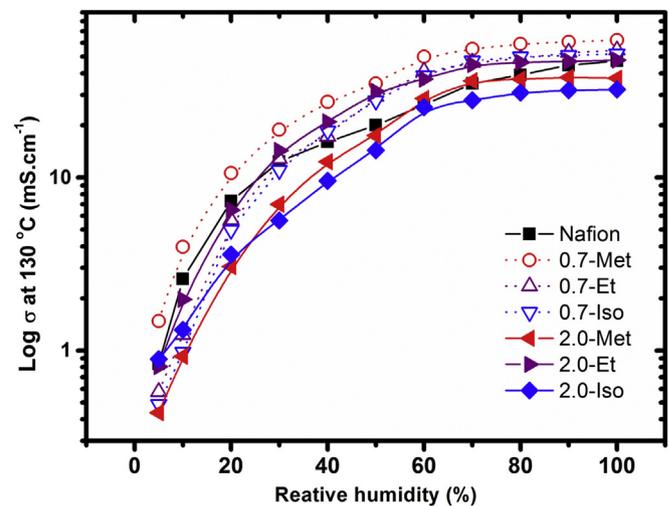


Fig. 5. Proton conductivity of Nafion and hybrids at 130 °C as function of the relative humidity.

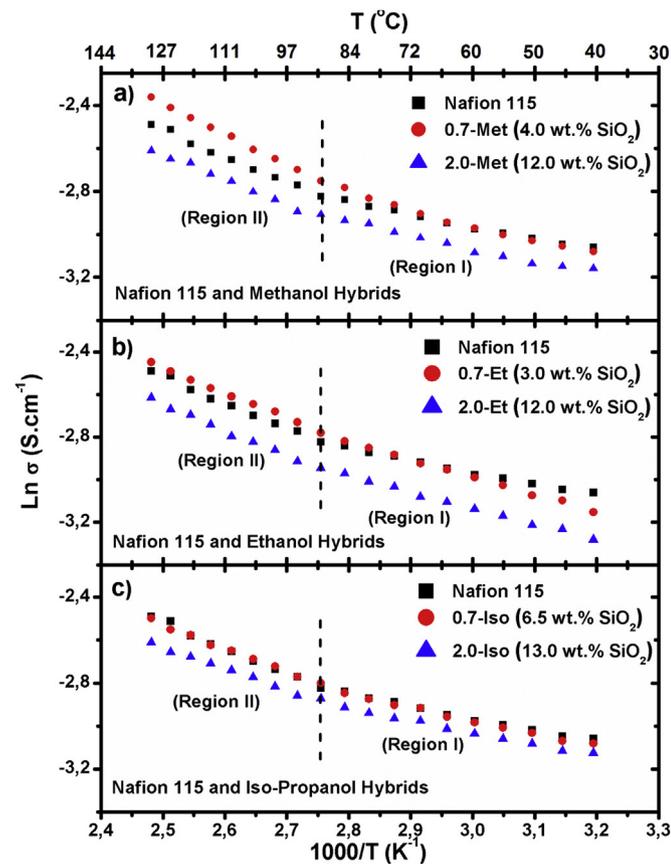


Fig. 4. Temperature dependence of the natural logarithm of the electrical conductivity for Nafion-SiO<sub>2</sub> hybrids synthesized in (a) Methanol; (b) Ethanol; and (c) Iso-propanol, measured at  $RH = 100\%$ . Electrical conductivity data for Nafion 115 are also presented. The numbers of the temperature scale on the top are rounded to the closest integer.

( $RH = 100\%$ ), the conductivity progressively increases within a broad temperature interval ( $180^\circ\text{C} > T > 30^\circ\text{C}$ ) [18], exhibiting a marked upturn at  $T > 90^\circ\text{C}$  [18,31], similarly to the data in Fig. 4. Moreover, silica is assumed to have minor contribution to the proton transport mechanism, and thus, the observed deviation of the low-temperature (region I) Arrhenius behavior has been attributed to the properties of the ionomer matrix. In the region (I), the dependence of the proton conductivity of hybrids and Nafion presents similar slopes, indicating that the predominant mechanism for proton transport is structural diffusion [18,22]. In general, the SiO<sub>2</sub>-rich hybrids ( $>12$  wt%) have lower conductivity values than unmodified Nafion, despite of higher water uptakes. This conductivity decrease can be a result of the increased volume fraction of the less conducting inorganic phase in the ionomer matrix [11]. It is worth mentioning that as showed in Tab.1 the water uptake was not significantly increased with increasing the silicon dioxide fraction. On the other hand, Nafion-SiO<sub>2</sub> hybrids with low silica content display higher proton conductivity than Nafion, a feature more marked at high temperature, indicating that the increased water uptake due to silica nanoparticles contributes to the proton conductance of hybrid electrolytes. As revealed by SAXS/SANS analysis the increase in the silica incorporation can increase the degree of connectivity of the inorganic phase in Nafion matrix, which can block more effectively the proton conducting sites. The highest proton conductivity at high temperature was obtained with Nafion-SiO<sub>2</sub> hybrid prepared in methanol. Such a high conductivity is probably a result of the structural properties inferred from SAXS/SANS data such as the high dispersion of the inorganic phase and the interaction with between the inorganic phase and the matrix ionic phase.

The dependence of proton conductivity on the relative humidity at high temperature is shown in Fig. 5. The conductivity dependence on the relative humidity observed for Nafion and Nafion-SiO<sub>2</sub> (Fig. 5) are very similar to the data reported for Nafion and Nafion hybrids [28]. The 0.7-hybrids present higher proton conductivities than both Nafion and 2.0-hybrids. The lower conductivity of 2.0-hybrids, similarly to the proton conductivity measurements of Fig. 4, is associated with the lower contribution of the silica to the proton transport. Silica is an insulating phase and an excess of this component contributes to a negative effect in the electrical conductivity. Notably, the hybrid membrane 0.7-Met (4% SiO<sub>2</sub>) exhibits superior proton conductivity at any measured relative humidity

levels. However, the opposite was observed for the 2.0-Iso hybrid membrane (13% SiO<sub>2</sub>), which exhibits conductivity values far below of the other membranes. It is important to note that the SAXS/SANS spectra of hybrid membranes revealed specific interactions of the inorganic phase with the Nafion conducting phase in the samples prepared in ethanol, whereas the samples prepared in isopropanol can promote agglomeration of the inorganic phase. Such features reflect directly on the proton conductivity dependence on the relative humidity.

Based on the combined experimental analysis, it can be inferred that ethanol and methanol solvents result in more homogeneously distributed silica, while isopropanol favors more agglomerated particles. Nevertheless, irrespectively of both the weight fraction and the localization of silica, the structural properties of the polymer matrix are essentially preserved. The silica phase prepared in methanol solvent was shown to be localized preferentially in Nafion ionic phase with a uniform dispersion along the polymer matrix promoting an improvement of the electrical properties of Nafion.

#### 4. Conclusions

Combined small-angle X-ray and neutron scattering data showed that the structural properties of Nafion, such as spatial distribution of ion-rich clusters and crystallinity, are well preserved when using the sol–gel synthetic route for the preparation of Nafion-SiO<sub>2</sub> hybrid membranes. Nafion-silica hybrids with improved properties can be achieved by a selection of a suitable solvent. The different affinities of alcohols by the ionomer matrix promoted the nucleation and growth of silica in different domains of Nafion, which resulted in hybrids with characteristic morphologies. Silica addition in the methanol media can promote improved properties, such as water uptake and proton conductivity at high temperatures as compared to unmodified Nafion. A detailed analysis of the Nafion-based hybrid membranes by scattering techniques indicated that the inorganic phase plays an important role and influences the properties of the polymer matrix depending on the particle dispersion, weight fraction, and localization in the structure of Nafion.

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