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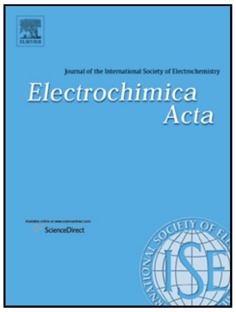
Journal of the International Society of Electrochemistry

Electrochimica Acta

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PII: S0013-4686(12)01498-3
DOI: doi:10.1016/j.electacta.2012.09.036
Reference: EA 19271

To appear in: *Electrochimica Acta*

Received date: 25-6-2012
Revised date: 10-9-2012
Accepted date: 13-9-2012

Please cite this article as: M.A. Dresch, R.A. Isidoro, M. Linardi, J.F.Q. Rey, F.C. Fonseca, E.I. Santiago, Influence of sol-gel media on the properties of Nafion-SiO_2 hybrid electrolytes for high performance proton exchange membrane fuel cells operating at high temperature and low humidity, *Electrochimica Acta* (2010), doi:10.1016/j.electacta.2012.09.036

Influence of sol-gel media on the properties of Nafion-SiO_2 hybrid electrolytes for high performance proton exchange membrane fuel cells operating at high temperature and low humidity

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Abstract

The effects of alcohol used as solvent during the sol-gel synthesis of Nafion-SiO_2 hybrid electrolytes have been evaluated. The alcohol controls the distribution of silica particles in the phase separated structure of Nafion and both the silica content and the water uptake of hybrid membranes are dependent on the alcohol solvent. Thermal and structural properties inferred from differential scanning calorimetry and small angle X-ray scattering were correlated with the enhanced water uptake and the proton conductivity of hybrid membranes. Accordingly, fuel cell tests carried out at 130 ºC and low humidity evidenced the superior performance of Nafion-SiO_2 hybrids.

Keywords: Nafion-SiO_2; PEM fuel cell; Hybrid Electrolytes; Sol-Gel Synthesis.

1. Introduction

Several electrolytes have been pointed out as possible alternatives for Nafion in proton exchange membrane fuel cells (PEMFCs) operating at high temperature [1,2]. However, the excellent physicochemical properties of Nafion have sustained its position as the standard PEMFC electrolyte. Numerous studies involving the synthesis and characterization of Nafion-based composite electrolytes aiming at stable high-temperature PEMFCs have been reported [3,4,5,6]. Nevertheless, some key issues such as the influence of both synthesis parameters and interactions between the polymeric matrix and the inorganic phase on the properties of Nafion-based composites are still a matter of debate.

The phase separated structure of Nafion, resulting from the incorporation of sulfonic groups in the PTFE backbone, combines both hydrophobic and hydrophilic characteristics [7]. The hydrophilic ionic clusters, resulting from the structural arrangement of the sulfonic groups, confer to Nafion a remarkable capacity of water absorption and provide the conducting paths for proton transport across the polymer [8]. Some structural models have been described to elucidate the morphology and the proton transport mechanism of Nafion; however, the non-periodic morphology and the nanophase separation still hinders a complete understanding of Nafion structure in a wide length scale range [7,9,10]. Recently, SAXS (small-angle X-ray scattering) data showed a network of parallel ionic clusters connected as inverted cylindrical micelles with ~4 nm diameter in hydrated specimens [11].

In Nafion-based hybrids, depending on the distribution of inorganic phase in the different regions of Nafion structure, the oxide particles can influence the polymer morphology and consequently, key properties for the fuel cell performance such as hydrophilicity and proton conductivity. Therefore, both structure and properties of Nafion-matrix composites are strongly dependent on the synthesis technique. Nafion-SiO_2 membranes have been produced by two main routes [2]: *i)* recasting (composite membranes) [12] and *ii) in situ* sol-gel synthesis (hybrid membranes) [13]. In the sol-gel methodology, Nafion acts as a template for hydrolysis/condensation reactions of tetraethyl orthosilicate (TEOS), catalyzed by the sulfonic acid groups into Nafion hydrophilic clusters [14,15]. The solvent employed in the sol-gel synthesis promotes the swelling of the Nafion matrix, allowing the polymer to absorb the oxide precursor. Therefore, different chemical interactions between the solvent and the polymeric matrix, such as different absorption levels of distinct types of alcohol by Nafion, can influence the properties of hybrid membranes [16,17,18].

In this context, Nafion-SiO_2 hybrids were produced by an optimized *in-situ* SiO_2 sol-gel method into Nafion 115 membranes using different alcohol solvents (methanol, ethanol, and 2-propanol). The Nafion-SiO_2 hybrid membranes were characterized aiming at their use as high temperature PEMFC electrolytes. The main results showed that the alcohol solvent has a significant effect on the general properties of the hybrid electrolyte, which resulted in enhanced performance of PEMFCs operating at high temperatures (130 ºC) and different relative humidity (RH) conditions.

2. Experimental

Nafion-SiO_2 hybrids were produced using commercial Nafion 115 membranes (127 µm thickness, DuPont). Firstly, membranes were treated in hydrogen peroxide solution (3% v/v) at 80 ºC for 1 h to eliminate organic impurities, followed by rinsing with water in the same conditions to remove H_2O_2 traces. Then, Nafion membranes were treated with sulfuric acid 0.5 mol L^{-1} solution at 80 ºC for 1 h, with subsequent washing in water to eliminate acid residues.

Prior to the sol-gel synthesis, Nafion 115 membranes were dried at 105 ºC for 24 h in a vacuum oven. Then, the membranes were immersed in an alcoholic solvent for 30 minutes in a closed vessel to allow the swelling of Nafion. Three distinct alcohols were used as solvents: methanol, ethanol, and 2-propanol. Then, the silica precursor (tetraethyl orthosilicate, TEOS – Aldrich) was added to a final concentration of 0.7 mol L^{-1} and kept for 30 minutes. The hydrolysis reaction of TEOS was carried out by acid catalysis using nitric acid (0.5 mol L^{-1}) at 50 ºC for 30 min. The membranes were removed from the reaction medium and the condensation reaction was carried out at 95 ºC for 24 h. Finally, the resulting membranes were exhaustively treated in H_2SO_4 0.5 mol L^{-1} and water at 80 ºC to remove residues and unstable particles. The SiO_2 incorporation degree in the hybrids was defined using the following expression: Δ_{SiO2} (%) = $(m_N - m_H)/m_N$, where m_N is the unmodified Nafion mass; m_H is the mass of the membrane after incorporation of the silica. The determination of the mass of the membranes followed the sequence: *i)* drying of the membranes in a vacuum oven at 95^oC for 24 h; *ii)* cooling down until room temperature (25^oC) under vacuum for 12 h; and *iii)* weighting of the membranes. A sample prepared in ethanol with a higher TEOS concentration (1 mol L^{-1}) was prepared following the same procedure exclusively for comparing the water uptake values. Nafion reference samples were prepared for each alcohol solvent by following the same procedure used for the fabrication of hybrids, but without adding the silica precursor (TEOS).

The water uptake was defined as Δm (%) = $(m_S - m_D)/m_D$, was evaluated by weighing the dry membrane (m_D) after thermal treatment at 110 ºC for 24 h in vacuum, and the water saturated membrane (m_S) after boiling it in water for 1 h. After the drying treatment membranes were allowed to cool down to room temperature while monitoring the weight; the m_D was determined when the measured value was constant at room temperature. The same procedure was used for the m_S of water saturated membranes, but in this case the excess water on the surface was removed by using a qualitative filter paper before weighing. The alcohol uptake of Nafion was determined following the same procedure, using alcohol at room temperature instead of boiling water. Both the water and alcohol uptakes were determined after three independent measurements.

Thermogravimetric (TG) analyses were performed between room temperature and 250 °C with a 10 °C min^{-1} heating rate under air flow (50 mL min^{-1}) in a Setaran Labsys. Differential scanning calorimetry runs (DSC, Mettler/Toledo model DSC 822) of water saturated samples were carried out in the 20 ºC to 180 ^{o}C temperature range at 20 ^{o}C min^{-1} heating rate in flowing N_2. Scanning electron microscopy (SEM) analyses (Leo model 440i) were carried out in carbon sputtered surfaces of fractured cross sections of membranes. Energy dispersive X-ray (EDX) analyses were used to determine the presence of Si along the cross section of hybrid membranes with a solid state detector Oxford Si(Li) using beam electron scanning at 12 keV.

The proton transport properties of the Nafion-SiO_2 specimens were studied by two-probe electrochemical impedance spectroscopy (EIS) measurements (through-plane direction) with a Zahner IM6 electrochemical workstation, with an applied excitation of 100 mV, in the 100 Hz to 1 MHz frequency interval. The EIS measurements were performed using a home-made sample holder, which consist of two connected stainless steel chambers, a water reservoir (down compartment) and the sample holder itself (up compartment), separated by a teflon thermal insulating ring. Both chambers are equipped with thermocouples and independent temperature controllers allow the control of the RH by the difference of water vapor pressure. The EIS data were collected in the 40 ºC – 130 ºC temperature range with 100% relative humidity (RH).

Small angle X-ray scattering (SAXS) experiments were carried out using synchrotron radiation at the Brazilian National Synchrotron Light Laboratory (LNLS). Experiments were conducted with an incident wavelength $\lambda = 1.488$ Å in the range of the scattering vector $q \sim 0.02 - 0.35$ $Å^{-1}$ ($q = 4 \pi \sin\theta / \lambda$, being 2θ the scattering angle). Scattering patterns from all samples were collected with MarCCD detector and the intensity curves were corrected for parasitic scattering, integral intensity and sample absorption with FIT2D software. Small angle X-ray scattering measurements were performed on dry and water saturated samples. Water saturated and dried samples were obtained by keeping the samples immersed in water during 24 h and treating them in a vacuum oven at 105 ºC for 24 h, respectively.

Catalyst layers of gas diffusion electrodes for single PEMFC were prepared as described previously [19]. The total metal loading was 0.4 mg cm^{-2} for both anode and cathode (Pt/C 20 wt.%, E-Tek). In all cases, 35.5 wt.% of Nafion (5 wt.% solution in a mixture of alcohols, DuPont), which corresponds to 1.1 mg cm^{-2}, was applied to the catalyst layer. The gas diffusion layer consisted of carbon powder (Vulcan XC-72R, Cabot) with 15 wt.% polytetrafluoroethylene (PTFE, TE-306A, DuPont) deposited onto a carbon cloth substrate (E-Tek). The thicknesses of the GDL and of the catalyst layer are 300±14 µm and ~13 µm, respectively. The membrane-electrodes assemblies (MEA) were fabricated by hot pressing the anode and the cathode to the electrolyte membranes (hybrids or Nafion 115) at 125 °C and 1000 kgf cm^{-2} for 2 min.

Fuel cell polarization measurements were carried out galvanostatically with a 5 cm^2 single cell with serpentine gas flow pattern. Fuel cells were fed with hydrogen and oxygen at flow rates of 440 mL min^{-1} and 380 mL min^{-1} respectively. The gases were saturated with water by gas humidifiers. The polarization curves were taken at different temperatures upon heating in the 80 and 130 ºC temperature range with total absolute pressure of 3 atm and 100% of RH. At 130 ºC, reduced RH conditions (75% and 50%) were set by controlling the gas humidifiers temperature, following the procedure described elsewhere [20,21]. Prior to data acquisition at each temperature and RH, the system was maintained at 0.7 V for 2 h in order to reach the steady-state condition.

3. Results and discussion

Table 1 displays values of alcohol and water uptake for Nafion, and silica weight fraction and water uptake for Nafion-SiO_2 hybrids synthesized with different alcohols. The swelling of the Nafion membrane during the sol-gel synthesis due to the alcohol solvent is mirrored by the alcohol uptake, which is supposed to play a key role in allowing an effective absorption of the oxide precursor by the polymer. Silica weight fractions varied from 3.0 to 6.5 wt.% depending on the solvent used. The hybrid with highest silica content (6.5 wt.% in 2-propanol) agreed with the highest alcohol uptake (97%) of Nafion, but such correlation was not observed for ethanol and methanol. Such a result demonstrated that physicochemical properties of the solvents other than the alcohol uptake by Nafion are important for the sol-gel synthesis. Amongst relevant solvent properties, the molar volume (V_m) was previously correlated with the increased thickness of swelled Nafion membranes [22]. In the present study, V_m showed some correlation with the silica content incorporated into Nafion. Both ethanol (V_m =58 cm^3 mol^{-1}) and methanol (V_m =40 cm^3 mol^{-1}) have comparable silica weight fraction (3 and 4 wt.%, respectively), whereas 2-propanol has the highest V_m=76 cm^3 mol^{-1}, which agrees with the highest silica incorporation measured .

Hybrid samples exhibited significantly increased water uptake in comparison to unmodified Nafion. However, it is interesting to note that no direct relation between silica weight fraction and water uptake was observed. Previous studies have used spectroscopic techniques such as electron spin resonance and nuclear magnetic resonance, along with dynamic light scattering (DLS) and small angle scattering techniques to investigate the structure of Nafion. Such studies revealed that different alcohols have distinct interactions with both the PTFE backbone and the ionic clusters of the ionomer [23,24,25]. It was found that alcohols penetrate in the perfluorinated regions and DLS studies of Nafion solutions in different alcohols pointed a high affinity of 2-propanol for the nonionic regions (hydrophobic PTFE backbone) [23]. Moreover, a marked partitioning effect between the ionic and nonionic regions of the

Nafion indicated that alcohols have a higher affinity for hydrophobic nonionic regions of Nafion, as evidenced from both small-angle neutron scattering (SANS) and positron annihilation studies [17,18]. Methanol and 2-propanol were observed to have the strongest partitioning effect, while ethanol exhibited a less pronounced partitioning. Such results suggest that different alcohol solvents can promote distinct access of the silica precursor inside the ionomer, resulting in different distributions of silica particles into Nafion. Particles synthesized by the sol-gel method are preferably formed in the ionic clusters [13]. However, due to both the alcohol partitioning in Nafion and the added nitric acid for the sol-gel synthesis, the alcohol solvents possibly promote the formation of a fraction of particles outside the ionic cluster, a feature more appreciable for alcohols with a strong interaction with hydrophobic regions of the polymer, such as 2-propanol. Accordingly, in 2-propanol a higher silica content is expected, while in ethanol silica plays a more significant contribution to the water uptake, in agreement with data shown in Table 1.

The water uptake gives further insights into the effects of the alcohol solvent on the hybrids. To further compare the effects of the alcohol solvent a specimen with ~6 wt.% of silica was fabricated in ethanol by using a higher concentration of the TEOS precursor (1 mol.L^{-1}). The water uptake of samples with similar silica content (~6 wt.%) produced in different alcohols (2-propanol and ethanol) were analyzed. As indicated in the Table 1, samples prepared in ethanol exhibited the highest water uptake, but a relatively small increase of the water uptake, from 45% to 48%, was measured when the silica content doubled from 3 wt.% to 6 wt.%, respectively. On the other hand, samples with similar silica weight fraction (6.5 wt.%) prepared in 2-propanol have a considerably lower water uptake (38%). Therefore, experimental results revealed that the silica content was not the only parameter controlling the enhancement of water uptake and indicated that the distribution of silica into the Nafion matrix, influenced by the alcohol solvent, plays a significant role in the process. Alcohols, such as 2-propanol, probably have a considerable fraction of inorganic particles far from the ionic clusters that are expected to make a lesser contribution to the water uptake. The water uptake of Nafion reference samples (without silica addition) for each alcohol solvent was analyzed. Measurements of water uptake shown in Table 1 revealed that the reference samples (prepared without the silica precursor) do uptake water similarly as Nafion (~30wt.%), demonstrating that the increased water uptake measured for hybrids was associated with the inorganic particles.

The Figure 1 shows typical SEM image and the correspondent EDX analysis of the cross section of a hybrid membrane. As observed from images displayed in Fig. 1, Si is homogenously distributed along the membrane thickness. Similar microstructures were observed in samples produced with different alcohol solvents (not shown), indicating that the sol-gel synthesis resulted in an effective incorporation of silica into the bulk of Nafion 115 membrane without any significant microstructural changes in the polymeric matrix or compositional gradients along the membrane.

The thermal properties of hybrids were investigated. Thermogravimetric (TG) runs (not shown) up to 250 °C revealed that hybrid samples have thermal behavior similar to Nafion irrespectively of the silica content and no significant thermal degradation was observed in the studied temperature range. The thermal properties of Nafion and hybrids were further investigated by DSC measurements shown in Figure 2. It is well known that Nafion undergoes a transition related to the ionic clusters usually ascribed as the ! relaxation occurring at $T_!$ ~100 °C, which is the onset of considerable molecular mobility [26,27,28,29]. The operation of PEMFC above $T_!$ induces undesired mechanical and/or dimensional instabilities in Nafion, which limits the application of such electrolytes at higher temperature [20,27]. The unmodified Nafion sample presented an endothermic peak at T = 85 °C, associated with the $T_!$ of hydrated H^+-form of the ionomer [26]. An appreciable shift to higher temperatures of such endothermic peak was observed for hybrid samples. The $T_!$ values increased with increasing SiO_2 weight fraction, reaching $T_!$ = 133 °C for the 2-propanol hybrid (6.5 wt.% SiO_2), a value ~50 °C higher than the one for Nafion. The increased $T_!$ of hybrid samples is probably related to the addition of inorganic nanoparticles in the polymeric matrix. Silica nanoparticles act as pinning centers that inhibit the long range mobility of the polymeric chains providing enhanced stability for the electrolyte of high-temperature PEMFCs [20,28]. Therefore, the structure of hybrid samples was further investigated by small angle X-ray scattering (SAXS) measurements.

Figure 3 shows the SAXS patterns of dry samples of both the pristine polymer and hybrids prepared with different alcohols. The main features of previously reported SAXS data for Nafion were confirmed: a first maximum at q ~0.005 nm^{-1} attributed to the crystalline phase (the nonionic PTFE hydrophobic backbone) and a second maximum at higher q ~0.023 nm^{-1} ascribed to the hydrophilic ionic clusters, which corresponds to a correlation distance roughly estimated by $D = 2\pi / q$ = 2.7 nm.[30,31,32,33,34].

The results showed that the additional scattering due to the inorganic particles contributed to more convoluted SAXS patterns of the Nafion-SiO_2 samples. Nevertheless, the main observed features of the SAXS patterns of hybrids were the characteristic peaks of the Nafion matrix along with an additional upturn at low $q \leq 0.003$ nm^{-1}. Such upturn can be related to a larger correlation distance between silica particles (roughly estimated to be D ~20 nm), but, more likely, the low q upturn is related to agglomerated silica particles with a characteristic diameter similar to this correlation distance. Thus, such agglomerates have dimensions incompatible with the ones of the ionic cluster [14] and are probably located outside the ionic clusters. It is expected that high silica content samples have a more significant fraction of agglomerates. The main contribution of such agglomerates to the properties of hybrid samples is possibly associated with the increased $T_!$ observed in DSC measurements (Fig. 2), a feature more evident in the 2-propanol sample [20,27,28].

On the other hand, the observed ionomer peak broadening of hybrids can be associated with the scattering of silica particles with characteristic diameter compatible with the dimensions of the ionic clusters (D ~3 nm), a feature of the sol-gel method that uses the ionic clusters as a template for the nucleation of inorganic particles. Such particles are expected to contribute more effectively with the enhanced water uptake of hybrids. Indeed, the sample prepared in ethanol exhibited a very broad ionomer peak in agreement with the measured high water uptake. The methanol hybrid exhibited the matrix peaks at essentially the same q values found for Nafion, indicating that a less significant distortion of the matrix structure occurred. However, for both, ethanol and 2-propanol samples, the crystallite peaks (q ~0.005 nm^{-1}) were slightly shifted to higher q values, representing a reduction of the correlation distance of crystallites that could be attributed to a more constrained structure due to the silica particles. The hybrid synthesized in 2-propanol displayed an additional correlation peak at q ~0.014 nm^{-1}, indicating a concentration of particles with intermediate correlation distance between the ones of crystallites and ionic clusters. Indeed, such alcohol is the one with a higher affinity for the nonionic regions and was observed to have a pronounced alcohol uptake by Nafion (97 wt.%) [23]. Thus, samples prepared with 2-propanol had the highest content of silica, being an noticeable fraction of the nanoparticles located outside the ionic clusters, in accordance with the properties observed for this hybrid, such as high $T_{!}$ and low water uptake.

Further details regarding the structure of hybrids were studied by SAXS experiments performed under controlled humidity. Figs. 4a and 4b show the evolution of SAXS patterns of Nafion and hybrid synthesized with methanol in both dry and water saturated (wet) conditions, respectively.

The main feature observed was the dependence of the position of the maximum corresponding to the ionic clusters on the water content. For the unmodified Nafion, the position of the ionomer peak shifted from 0.021 nm^{-1} (dry) to 0.015 nm^{-1} (water saturated). On the other hand, hybrids in wet conditions (Fig. 4c) showed a more pronounced shift to lower q ~0.011 nm^{-1}. A correlation distance of the ionic clusters D ~2.7 nm was found for all dried membranes, in agreement with previously reported values [35]. In water saturated samples the ionic cluster correlation distance of unmodified Nafion reached D ~4 nm while all hybrids exhibited larger values (D ~5.6 nm), irrespectively of silica weight fractions or water uptake of hybrids synthesized with different alcohols (Table 1). Such a marked expansion (swelling) of the ionic clusters is in agreement with the increased water absorption of hybrids displayed in Table 1 and added evidence to the localization of silica particles in the hydrophilic phase of Nafion.

The structural and thermal properties are reflected in the transport properties of the hybrid electrolytes. The proton conductivity ! was studied by impedance spectroscopy measurements in wet condition (RH=100%) in a wide temperature range. Figure 5 shows Arrhenius plots of the ionic conductivity of Nafion and hybrids synthesized with the different solvents. All samples exhibited a thermally activated Arrhenius-type ! (T) dependence, fitted to a straight line in the measured temperature range. At low temperatures, hybrids were found to have higher ! than unmodified Nafion, and the increase of SiO_2 weight fraction decreased ! . Such behavior was observed at temperatures up to ~100 °C and for T > 100 °C hybrids with low silica content (the ones synthesized in methanol and ethanol) and Nafion had comparable ! values up to 130 °C.

The activation energy (E_a) values were calculated from the fitted Arrhenius plots and listed in Table 2. The calculated E_a for Nafion-SiO_2 hybrids was slightly lower than the ones found for Nafion, suggesting that silica nanoparticles influence the charge transport mechanism; however, no direct dependence on the silica content was detected [36,37,38,39]. Previous studies on the proton conductivity of Nafion-SiO_2 hybrids have reported different behaviors, depending on both the measuring temperature and RH, and the silica weight fraction [36,38]. At relatively low silica content (< 10 wt.%), either silica-independent ! or increased ! with silica addition have been observed. Arguments for enhanced proton transport in silica hybrids have included the increased water uptake and a disruption of the long range Coulomb interaction between negative sulfonic groups and H^+ due to fixed positively charged silica particles [36]. Increased conductivity of cast Nafion-SiO_2 has also been related to increased polymeric chain mobility, as inferred from nuclear magnetic resonance experiments [40]. In the present study, the lower E_a of hybrids indicated that low volume fractions of silica nanoparticles facilitate the proton transport in the Nafion matrix. Such a result is probably related to both the higher water uptake and the ionic cluster size of hybrids that exhibited a more marked swelling upon hydration than Nafion according to SAXS data (Fig. 4). Recent simulations of proton transport in Nafion using random walk theory correlated the water content with increased size of ionic cluster, resulting in better connectivity between the ionic clusters and a higher probability for ion hopping [41]. The experimental data presented here are in agreement with this simulated scenario and suggest that silica addition changed the structure of aqueous domains allowing a better connectivity of the ionic clusters.

The hybrid membranes were tested in single PEMFC operating at both high temperature and low RH. Figure 6 shows polarization curves of PEMFC using Nafion and Nafion-SiO_2 electrolytes at 80 °C and 130 °C with RH=100%, and at 130 °C with RH= 75 and 50%. Nafion reference samples produced in different alcohols were also tested and exhibited similar performances; thus, for sake of clarity, only the polarization data of the reference sample synthesized in 2-propanol is included in Fig. 6a. The polarization curves of all reference samples exhibited a low performance mainly associated with higher ohmic drop (iR) and diffusional overpotentials. Such overpotentials are probably related to morphological changes of Nafion as a result of the interaction with the alcohol solvents [42]. Such results are strong evidence that the enhanced performance of hybrids is directly related to the addition of silica nanoparticles.

At low temperature (Fig. 6a), hybrids have a slightly superior performance than unmodified Nafion, a feature more evident in the region of ohmic drop overpotential, as displayed in Table 2. On the other hand, the performance of the unmodified Nafion was severely reduced with increasing operating temperature (130 °C), while hybrid samples practically sustained at 130 °C the performance measured at 80 °C, as shown in Fig. 6b. Polarization curves at high temperature with reducing RH from 100% to 50% (Figs. 6b-6d) confirmed the progressive degradation of Nafion with decreasing RH. More importantly, at low RH (75 and 50%) hybrids obtained in ethanol showed the highest power density, followed by 2-propanol and methanol hybrids. Nafion-SiO_2 electrolytes displayed remarkable improvements at high temperature and reduced RH depending on the alcohol used. Hybrids prepared in 2-propanol and methanol, which have higher SiO_2 content and lower water uptake than the ones prepared in ethanol, showed high performance in fully wet environment, whereas ethanol hybrids, with the highest water uptake, were more efficient under reduced RH. At 130°C and RH=75%, Nafion-SiO_2 hybrids prepared in ethanol and 2-propanol exhibited a maximum power density 45% higher than that of Nafion under the same operating conditions and equivalent to that of Nafion operating in optimal conditions (80 °C and RH=100%).

The enhanced fuel cell performance is mainly related to the transport properties of Nafion hybrids that involve complex diffusion processes in which the proton conduction is accompanied by water diffusion. Previous in-situ EIS data of fuel cells with Nafion-TiO_2 hybrids showed that hydrophilic particles can influence the water transport contributing to a more efficient water back-diffusion, which lowers the flooding effects at the cathode and enhances oxygen reduction reaction (ORR) kinetic [3]. The polarization data in Fig. 6 and the distribution of hydrophilic particles in the ionomer matrix indicated that the inorganic particles have a direct influence on both proton and water transport processes taking place in the hybrid electrolytes.

In general, properties exhibited by the synthesized hybrids, such as enhanced water uptake, thermal properties, and proton conductivity, contributed to improve the performance of the tested fuel cells. Such properties are closely related to an effective and homogenous incorporation of SiO_2 nanoparticles with an average size compatible with the dimensions of the nanophase separated structure of Nafion, as inferred from SAXS analysis. The experimental results indicated that different alcohol solvents influenced the interaction of silica particles with different structural phases of Nafion. Water uptake and SAXS data indicated that the silica fraction in the ionic clusters was comparable, irrespectively of both the alcohol used and the silica content. Such fraction of inorganic particles is supposed to contribute more effectively to the enhanced water retention and proton transport. In addition, thermal and structural properties of hybrid electrolytes, inferred from SAXS and DSC data, were also affected by silica particles in the nonionic regions of the polymer matrix. The combined properties resulting from the addition of silica contributed to a significant increase of the fuel cell performance at high temperatures and reduced RH that was associated with both enhanced proton transport properties and water management.

4. Conclusions

Nafion-SiO_2 hybrids were prepared by an optimized sol-gel route with different alcohol solvents. The experimental data indicated that silica nanoparticles are likely to have different fractions distributed in the nanophase separated structure of Nafion, depending on the alcohol solvent. The combined results showed that particles located in both the nonionic and ionic regions of the ionomer have important contributions to enhanced thermal stability and water uptake, respectively. Such features resulted in significant improvements of the PEMFCs using hybrid electrolytes tested at high operating temperature and low relative humidity that surpassed the maximum power density of Nafion at optimal conditions.

Acknowledgments

The authors are thankful to CNEN and the Brazilian agencies FAPESP, FINEP, and CNPq for the financial support and scholarships. Thanks are due to Dr. A.B. Lugão and MSc. H.A. Zen who helped us with DSC measurements.

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Tables

Table 1: Alcohol and water uptake for Nafion, SiO_2 incorporation degree, and water uptake for Nafion-SiO_2 hybrids and Nafion reference samples treated in different alcohols.

Sample	SiO_2 (wt.%)	Water uptake (wt.%)	Alcohol uptake of Nafion [Water uptake of reference Nafion] (wt.%)		
			Methanol	Ethanol	2-Propanol
Nafion	-	30 (2)	73 (3) [28 (2)]	92 (4) [30 (2)]	97 (4) [32 (2)]
Nafion-SiO_2 in Ethanol	3.0 (2)	45 (4)	-	-	-
Nafion-SiO_2 in Methanol	4.0 (2)	38 (3)	-	-	-
Nafion-SiO_2 in 2-Propanol	6.5 (3)	38 (3)	-	-	-
Nafion-SiO_2 in Ethanol (TEOS 1 mol.L^{-1})	6.0 (3)	48 (3)	-	-	-

Table 2: Activation energy values, proton conductivity, and specific area resistance of Nafion and Nafion-SiO_2 hybrids.

Sample	E_a (kJ mol^{-1})	Proton conductivity (σ cm^{-1})		Specific area resistance (Ω cm^{-2})	
		80 ºC	130 ºC	80 ºC	130 ºC
Nafion 115	11	0.058	0.095	0.26	0.28
Nafion-SiO_2 in Methanol	8.7	0.063	0.094	0.23	0.21
Nafion-SiO_2 in Ethanol	8.7	0.065	0.101	0.24	0.26
Nafion-SiO_2 in 2-Propanol	9.7	0.060	0.084	0.21	0.21
Nafion Reference in 2-Propanol	-	0.030	-	0.32	-

Figure Captions

Figure 1: (a) Fractured cross-section SEM image and (b) EDX mapping for Nafion-SiO_2 hybrid synthesized in methanol. The solid lines limit the thickness of the membrane.

Figure 2: Differential scanning calorimetry for Nafion and Nafion-SiO_2 hybrids synthesized with different alcohols.

Figure 3: Small-angle X-ray scattering for dry samples of Nafion and Nafion-SiO_2 hybrids synthesized with different alcohols. Intensity values were normalized.

Figure 4: Small-angle X-ray scattering for: (a) Nafion 115 and (b) Nafion-SiO_2 methanol hybrid dry and water saturated (wet), and (c) wet samples.

Figure 5: Arrhenius plots for Nafion and Nafion-SiO_2 hybrids synthesized with different alcohols. Straight lines represent the best linear fittings.

Figure 6: H_2/O_2 polarizations curves for Nafion and Nafion-SiO_2 hybrids synthesized in different alcohol solvents at a) 80 ºC with RH=100%, b) 130 ºC with RH=100%, c) 130 ºC with RH=75%, and d) 130 ºC with RH=50% . The polarization curve at 80 °C of Nafion 2-propanol reference sample is shown. The open symbols represent the polarization curves and the filled symbols correspond to the power density curves.

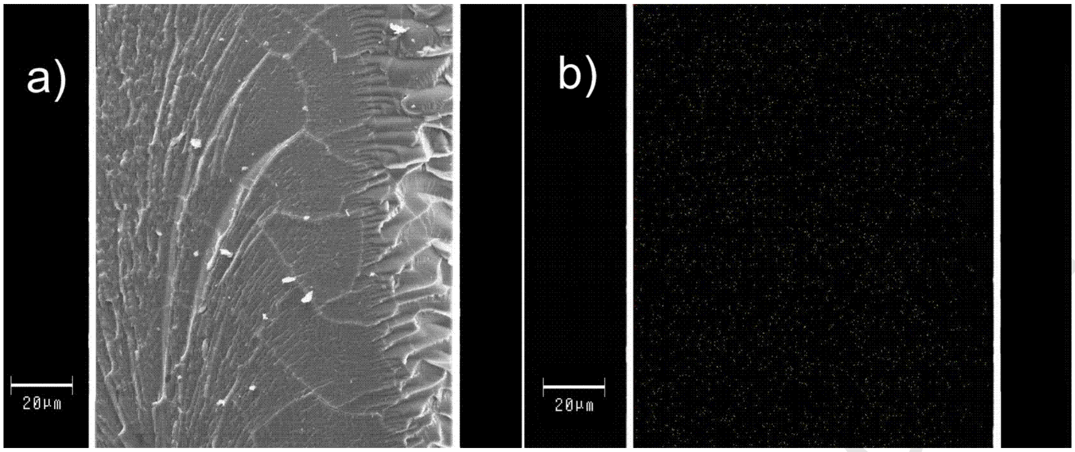


Figure 1

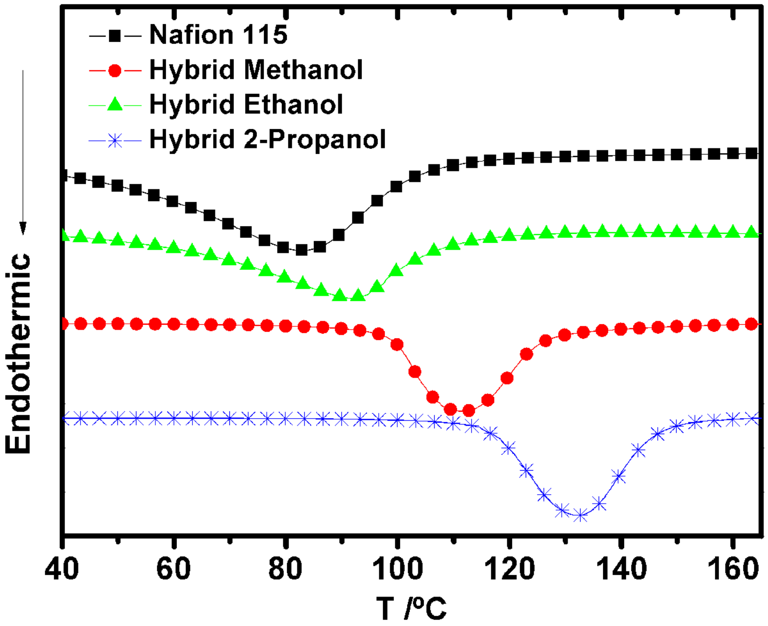
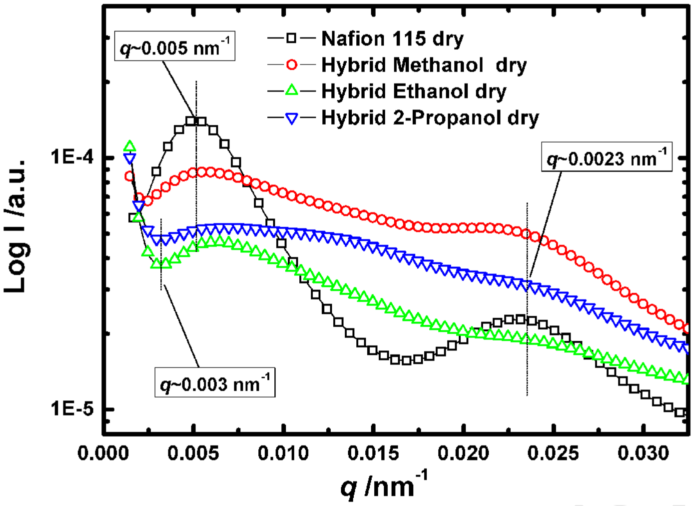


Figure 2



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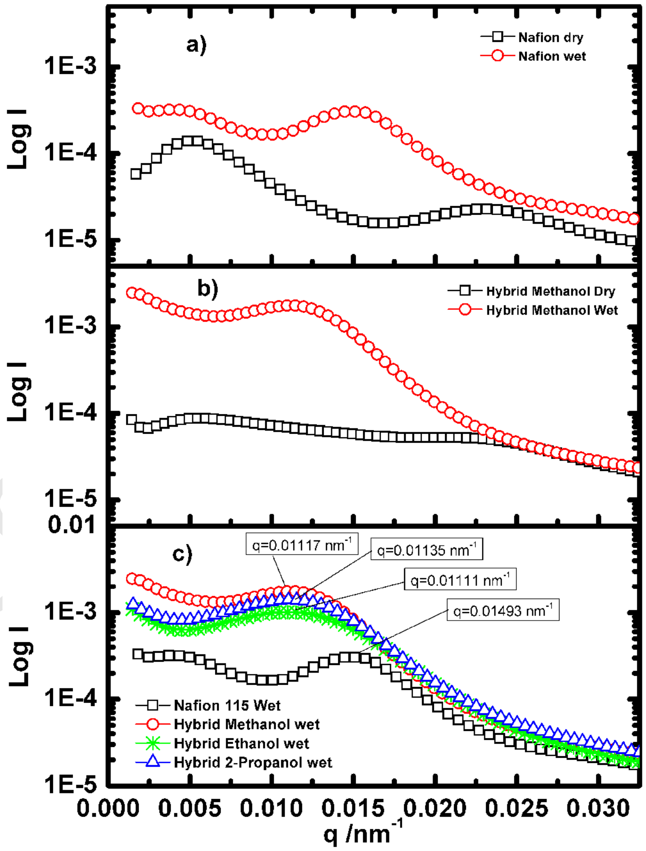

Figure 4

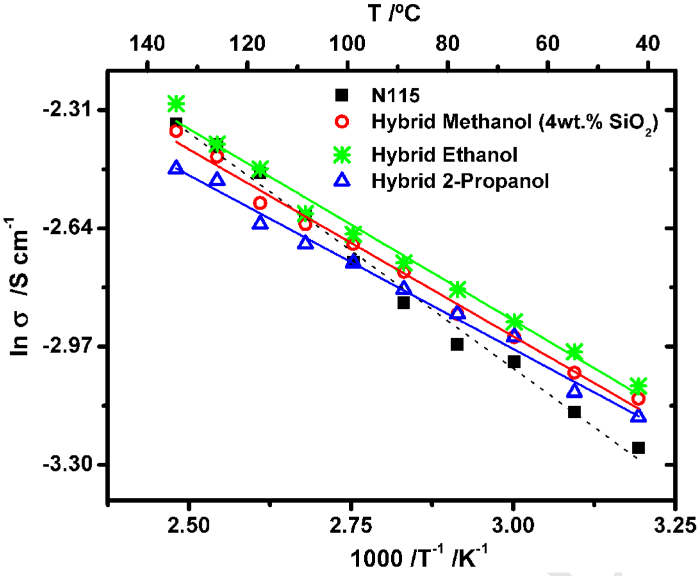

Figure 5

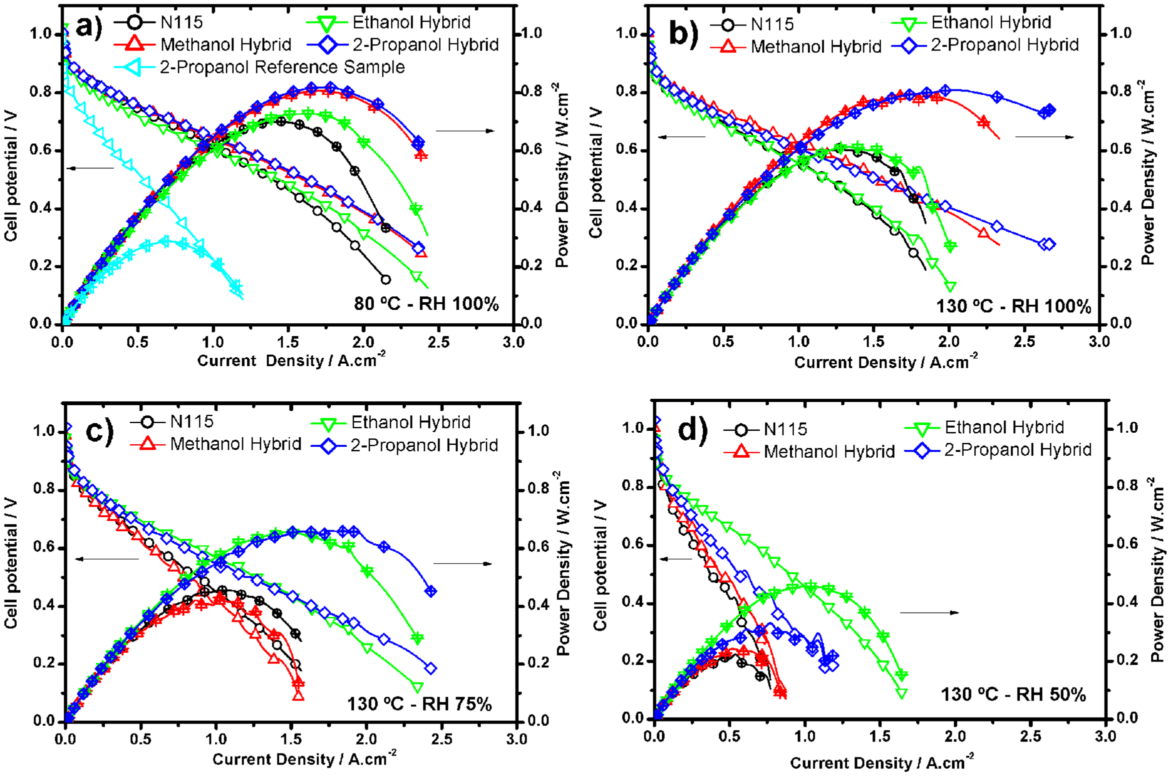

Figure 6