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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 °C and low humidity evidenced the superior performance of Nafion–SiO_2 hybrids.

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 [3–6]. 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 [16–18].

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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 °C) 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 °C 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 °C 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 °C for 24 h in a vacuum oven. Then, the membranes were immersed in an alcoholic solvent for 30 min 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 min. The hydrolysis reaction of TEOS was carried out by acid catalysis using nitric acid (0.5 mol L^{-1}) at 50 °C for 30 min. The membranes were removed from the reaction medium and the condensation reaction was carried out at 95 °C for 24 h. Finally, the resulting membranes were exhaustively treated in H_2SO_4 0.5 mol L^{-1} and water at 80 °C to remove residues and unstable particles. The SiO_2 incorporation degree in the hybrids was defined using the following expression: Δ_{SiO_2} (%) = $(m_N - m_H)/m_N$, 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 °C for 24 h; (ii) cooling down until room temperature (25 °C) 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 °C 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 20–180 °C temperature range at 20 °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–1 MHz frequency interval. The EIS measurements were performed using a homemade 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 40–130 °C 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 °C 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 °C temperature range with total absolute pressure of 3 atm and 100% of RH. At 130 °C, 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