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# Performance of Nafion-$TiO_2$ hybrids produced by sol-gel process as electrolyte for PEMFC operating at high temperatures.

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The fabrication and testing of Nafion-$TiO_2$ hybrid membranes as the electrolyte of proton exchange membrane fuel cell (PEMFC) are reported. A low temperature sol-gel process was used to effectively incorporate the hydrophilic anatase nanoparticles into the Nafion matrix. Fuel cell testing at temperatures up to 130 °C revealed that the hybrid membranes exhibit a higher ohmic drop when compared to Nafion. On the other hand, the hybrid membranes show an increased performance with increasing temperature and reduced relative humidity (RH). In addition, it was found that the inorganic phase confers stability to the polymer allowing for the operation at high temperature and reduced RH.

## Introduction

Proton exchange membrane fuel cell (PEMFC) has emerged as a promising electric supply system for stationary, vehicular, and portable applications. This device is based on the perfluorosulfonic acid membrane electrolytes such as Nafion®. However, these ionomeric electrolytes limit PEMFC operation at temperatures ~80 $^{o}$C. At higher temperatures, the strong dependence of the protonic transport on the water content of this ionomer results in drastic reduction of the conductivity that hinders the PEMFC operation. On the other hand, operation at higher temperatures, in the 130 °C - 150 °C range, would significantly boost PEMFC performance, enhancing important parameters such as electrode reaction kinetics and carbon monoxide (CO) tolerance, and allowing an easier water and thermal management [1]. Alternative polymeric electrolytes aiming to replace Nafion in PEMFC technology have been intensively investigated. Some materials, such as PBI, try to overcome the temperature limitation imposed by water in the Nafion-like membranes. However, the good proton conductivity and chemical stability of Nafion membranes make this polymer the standard electrolyte of PEMFC. In this context, the development of organic-inorganic hybrids based on Nafion and oxides with hygroscopic properties has been the focus on intense research, mainly, at intermediate temperatures (100 $^{o}$C -140 $^{o}$C).

Organic-inorganic hybrids are characterized by the insertion of hygroscopic oxides, such as $TiO_2$ [2,3], $SiO_2$ [4,5], and $ZrO_2$ [6], into the polymeric matrix, aiming to an enhanced humidification at high temperatures provided by the structural water retained in the inorganic phase. In general, the organic-inorganic hybrids are synthesized by *in-situ* incorporation of the oxide nanoparticles using sol-gel process into the pores of commercial Nafion membranes. Although the sol-gel methodology seems to be more adequate to produce oxides homogeneously dispersed, the leaching out of the inorganic phase during acid treatment affects the stability and the performance of these hybrids during operation. According to previous studies, this behavior may be attributed to an insufficient condensation of the hydroxides yielded during the hydrolysis reaction [3,8].

The objective of the present study is to produce stable Nafion-$TiO_2$ hybrids by *in-situ* sol-gel process at low temperature, and to evaluate such electrolytes in $H_2/O_2$ single fuel cell operating at high temperatures and different relative humidity (RH) conditions.

## Experimental

Nafion-$TiO_2$ hybrids were produced by *in-situ* synthesis of $TiO_2$ into commercial Nafion 115 membranes by sol-gel process using Ti-peroxy precursor. Nafion membranes were previously dried at 110 °C/24 h and immersed in absolute ethanol. In a closed vessel, the membrane was added to different quantities (1.0; 3.0; 5.0; and 10 mL) of a 30% ethanol solution of titanium tetraisopropoxide (TIP, Aldrich) for 1 h. The total volume of the solutions was adjusted to 22 mL by adding ethanol. In order to promote the formation of the Ti-peroxy sol, hydrogen peroxide was added in a $H_2O_2$:TIP molar ratio of 12:1. Then, the membrane-solution mixture was submitted to two consecutive heat treatments at 75 °C for 12 h in a closed and opened vessel for the formation of gel and precipitation of the nanoparticles, respectively[9]. Finally, all membranes were exhaustively treated in 0.5 $molL^{-1}$ $H_2SO_4$ and water at 70 °C to remove residues.

The hybrid membranes were characterized by ultraviolet-visible (UV-vis) spectroscopy, thermogravimetric analysis (TG), and X-ray diffraction (XRD). The UV-vis transmittance spectra for Nafion, Nafion-$TiO_2$ hybrids, and $TiO_2$ powders (P25, Degussa) were obtained by using spectrophotometer Cary 50 (Varian) in the 200-800 nm range. In order to evaluate the stability of the hybrids in acidic media, UV-vis spectra were also performed after exhaustive $H_2SO_4$ treatments. The weight fraction of $TiO_2$ in the Nafion matrix and the thermal response were evaluated by thermogravimetry (Setaram Labsys) in the temperature range of 25 °C to 800 °C with a heat rate of 10 °C $min^{-1}$ in air. X-ray diffraction patterns of the hybrids were obtained in a Multiflex (Rigaku) diffractometer, using Cu K$\alpha$ radiation in the 5° - 75° $2\theta$ range with scan rate 2° $2\theta$ $min^{-1}$.

The transport properties of the samples were studied by two-probe electrochemical impedance spectroscopy (EIS) measurements. EIS data were collected in the 25 °C - 80 °C temperature range with relative humidity (RH) ~ 98 % in the 100 Hz - 1 MHz frequency range with applied amplitude of 200 mV.

Catalyst layers of gas diffusion electrodes for single PEMFC were prepared as described previously [10]. 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) was applied to the catalyst layer. The gas diffusion layer consisted of carbon powder (Vulcan XC-72R, Cabot) with 15 (w/w) polytetrafluoroethylene (PTFE, TE-306A, DuPont) deposited onto a carbon cloth substrate (E-tek). Membrane and electrode assemblies (MEA´s) were prepared by hot pressing the anode and the cathode to the Nafion 115-based membranes ($H^+$, DuPont) at 125 °C and 1000 kgf $cm^{-2}$ during 2 min.

Fuel cell polarization measurements were carried out galvanostatically with a 5 $cm^2$ single cell using hydrogen and oxygen saturated with water. The polarization curves were taken with increasing temperature in the 80 °C - 130 °C range with total absolute pressure of 3 atm (100% RH). The stability of the fabricated membranes was evaluated by performing repeated measuring cycles up to 130 °C. Reduced RH conditions (75% and 50%) for polarization measurements were set by controlling the gas humidifiers temperature. Before data acquisition at each temperature, the system was previously kept at 0.7 V for 2 h in order to reach the steady-state condition.

## Results and discussion

UV-vis spectra (not shown) for $TiO_2$, Nafion, and hybrid membranes demonstrated the effective insertion of $TiO_2$ into the polymer for all studied TIP concentrations. In addition, the data revealed that the $TiO_2$ is preserved after the successive acid treatments of the polymer.

The $TiO_2$ weight fraction of the hybrid membranes, estimated by TG analyses, was found to be in the 3 wt.% - 9 wt.% range. As general trend, the $TiO_2$ weight fraction increases with increasing oxide precursor concentration, a feature that was reflected in the electrical properties of the samples. Fig. 1 shows the proton conductivity of the Nafion and Nafion-$TiO_2$ hybrids obtained with different TIP volumes. The experimental data evidenced that the conductivity of the membranes diminishes with the increase of the TIP concentration (volume). Such a decrease of the protonic conductivity is consistent with the addition of an insulating phase ($TiO_2$) into the polymer electrolyte. However, the data shown in the Fig. 1 evidenced that the percolation threshold of the inorganic phase was not attained up to the maximum concentrated TIP solution studied (10 mL). In addition, the temperature dependence of the electrical conductivity determined from the EIS diagrams revealed that the transport mechanism of the ionomer was not affected by the addition of the inorganic phase.

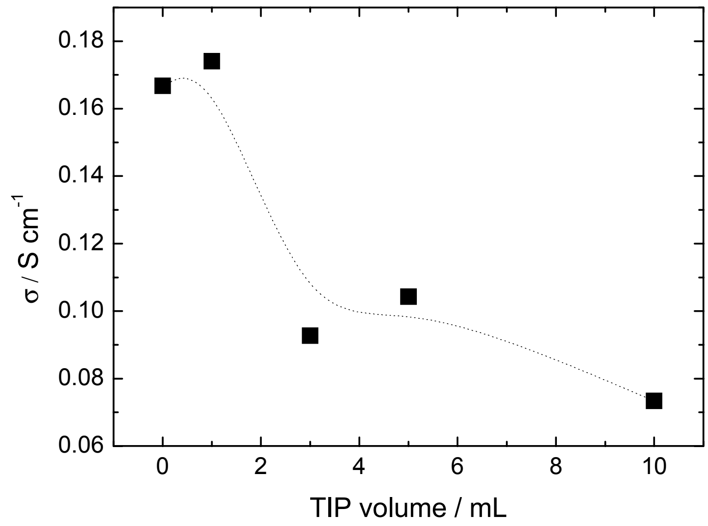

Fig. 1: Proton conductivity dependence on the $TiO_2$ precursor volume measured at T = 55 °C of Nafion (x = 0 mL) and Nafion-$TiO_2$ hybrids produced by Ti-peroxy sol-gel process. The dotted line is guide to the eye.

The Fig. 2 displays the XRD diffractogram for Nafion-$TiO_2$ hybrid (TIP 5 mL). All the observed diffraction peaks were indexed as belonging to Nafion and the $TiO_2$ anatase phase (JCPDS 21-1272). The average crystallite size was evaluated by Scherrer equation by using (101) Bragg's plane reflection [11]. The obtained value for the crystallite size (~6 nm) is consistent with the broad diffraction peaks observed. Moreover, such a nanometric particle size is comparable to the reported size of hydrophilic Nafion cavities [12], suggesting that the crystalline $TiO_2$ nanoparticles were inserted in the hydrophilic sites.

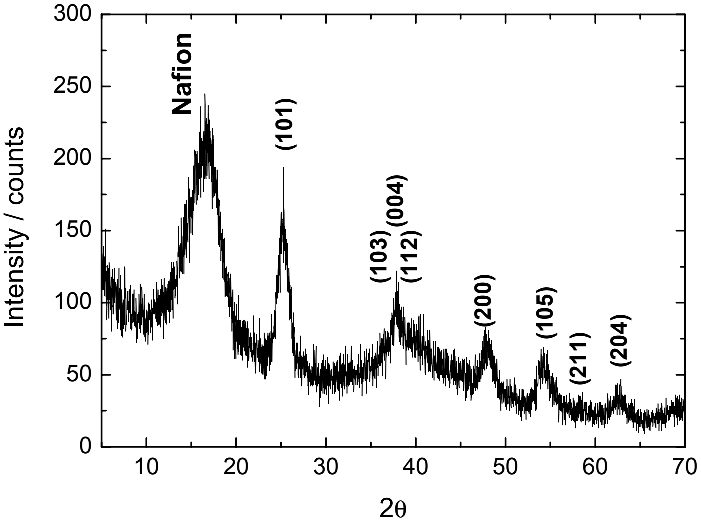

Figure 2: X-ray diffractogram for Nafion-$TiO_2$ hybrid prepared with the 5 mL TIP precursor. Indexed peaks refer to the $TiO_2$ anatase phase.

The characterization of the membranes evidenced that the Ti-peroxy sol-gel process was effective to incorporate anatase-$TiO_2$ nanoparticles into the Nafion matrix. Thus, the performance of the hybrid electrolytes was investigated in fuel cells operating up to 130 °C. The Fig. 3 displays the polarization curves for unmodified Nafion and the Nafion-$TiO_2$ membranes, with different $TiO_2$ contents, as a function of the cell temperature and RH.

The overall polarization performance of the Nafion-$TiO_2$ hybrids at 80 °C was lower than that of the unmodified ionomer. Such an effect is primarily associated with a higher ohmic drop overpotential due to the presence of the oxide nanoparticles in the hydrophilic pores of the polymeric matrix, in agreement with the conductivity data displayed in Fig. 1.

Figs. 3b-d illustrate that ohmic drop overpotential of the hybrid membranes increases with the increasing precursor concentration (Ti-peroxy), further indicating that the $TiO_2$ incorporation can be controlled by the TIP concentration in the sol-gel process. The fuel cell polarization curves for unmodified Nafion taken in the temperature range of 80 $^oC$ -120 $^oC$ are nearly temperature independent. On the other hand, at higher temperature and with decreasing RH the performance rapidly decays due to decreasing of the proton conductivity associated with water loss (Fig. 3a). Conversely, the hybrids show an increment of the performance when the temperature is increased from 80 °C up to 120 °C. Such a feature is clearly observed as a ~50% increase in the electrical current drawn at 600 mV in comparison to the ones obtained at 80 °C (Figs. 3b-d). An important feature to be discussed concerns the polarization curves measured at 130 °C as a function of the RH. In contrast to Nafion, the hybrid electrolytes are insensitive to the RH reduction from 100% to 75%, and the performance at such conditions is similar to that at 80 °C and 100% RH. In fact, the TIP= 5 mL membrane (Fig. 3 c) shows an appreciable increase of the polarization curve when the RH is reduced to 75%. Further decrease of the RH to 50% results in severe degradation of the fuel cell irrespectively the $TiO_2$ content.

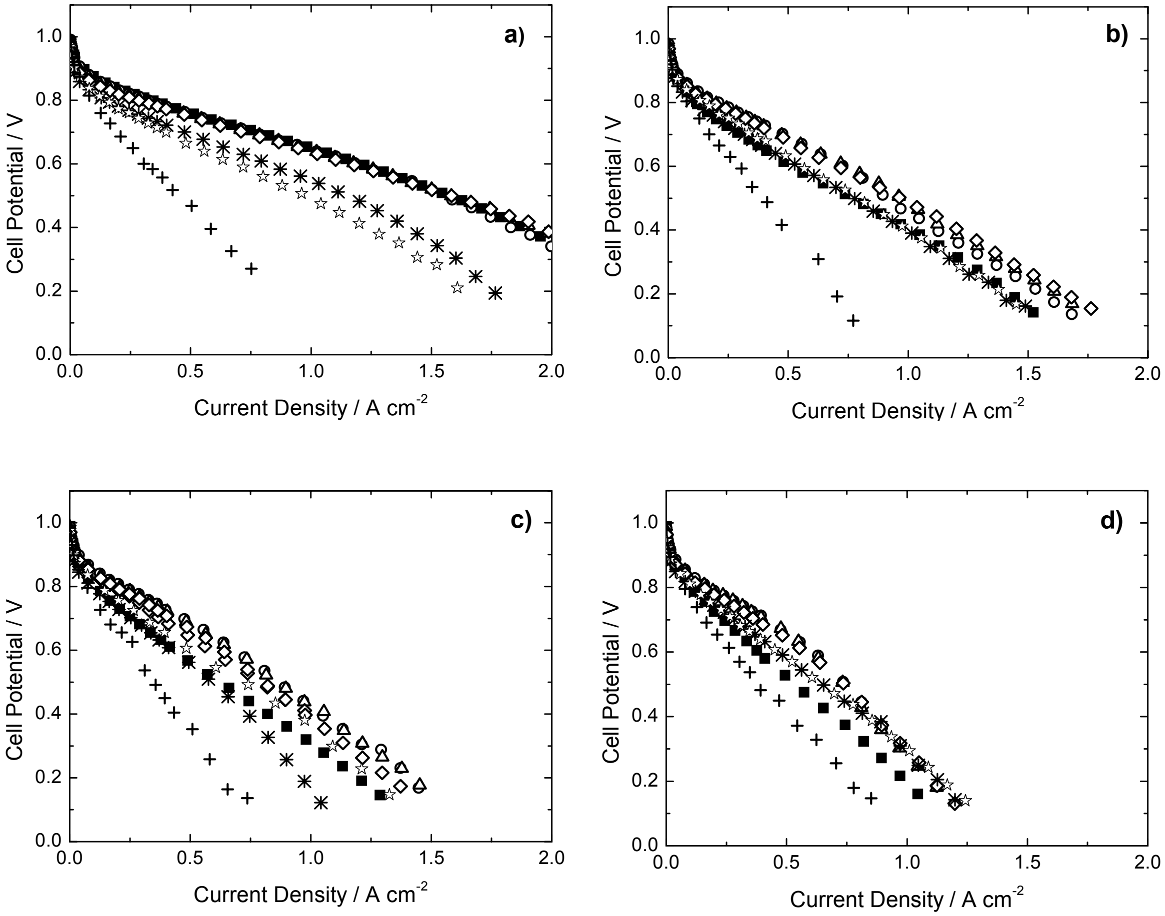

Fig. 3: $H_2/O_2$ polarization curves for: a) Nafion, b) Nafion-$TiO_2$ (TIP=3mL), c) Nafion-$TiO_2$ (TIP=5mL), and d) Nafion-$TiO_2$ (TIP=10mL) at (■) $80^{o}$C; (○) $100^{o}$C; (△) $110^{o}$C; (◇) $120^{o}$C; (✳) $130^{o}$C; (☆)$130^{o}$C RH=75%; and (+)$130^{o}$C RH=50%. Absolute pressure: 3 bar.

This behavior indicates that the $TiO_2$ incorporation into Nafion significantly changes the water management of the fuel cell. Similar features were previously reported and associated with a structural change of the oxide and an enhancement of the water content at high temperatures and reduced RH [13]. However, preliminary EIS experiments recorded during fuel cell operation suggest that the performance increase of the hybrids at 75% RH is more likely to be related to electrode processes than to an increase of the electrolyte conductivity. These experiments are underway and need further investigation in order to determine a more conclusive mechanism of the performance dependence on both the inorganic phase content and measurement conditions. Nonetheless, the observed features displayed in the Fig. 3 indicate that an optimized water management is an important feature for the improvement of the fuel cell performance using hybrid electrolytes at high temperature and low RH.

Previous studies [3,8] have raised concerns about the stability of oxide nanoparticles incorporated by sol-gel into Nafion during treatments in acid. Such a kind of treatment is a primordial step to promote both cleanness and the activation of the sulfonic acid groups of the Nafion membrane. However, $TiO_2$ nanoparticles resulting from an incomplete condensation of hydroxides produced by TIP hydrolysis reaction at room temperature can be leached out of the membrane upon acid treatment [8]. In the present study, the main advantage of the production of hybrid membranes by sol-gel process using Ti-peroxy precursor is that the hydrolysis process can be controlled by the TIP:$H_2O_2$ ratio and the heat treatment time at 75 °C. This method produces crystalline nanoparticles more stably incorporated to the polymeric matrix that can resist to exhaustive acid treatments, as indicated by the UV-vis analyses.

In order to further check the stability of the Nafion and Nafion-$TiO_2$ hybrids, polarization curves at 80 °C were measured before each measuring cycle from 100 °C up to 130 °C. The Fig. 4 shows the polarization curves for Nafion and Nafion-$TiO_2$ hybrid (TIP=3 mL) taken at the first measuring cycle and subsequent ones, which accumulate ~90 h of fuel cell operation at temperatures $\geq$ 100 °C and reduced RH.

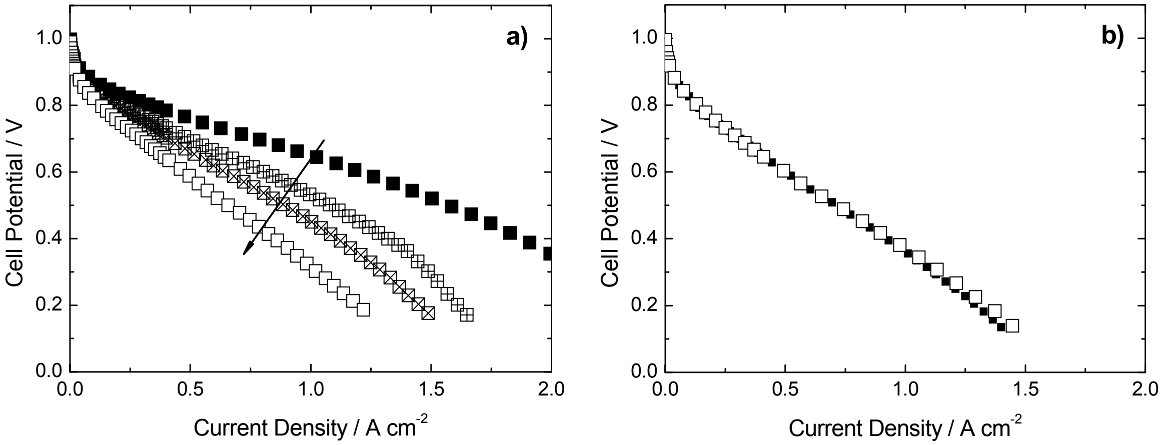

Fig. 4: $H_2/O_2$ polarization curves measured at 80 °C before (■) and after (□) 90 h of operation at high temperatures and reduced RH for fuel cells using: **a**) Nafion and **b**) Nafion-$TiO_2$ (TIP=3mL) hybrid. In Fig. 1 **a**), the arrow points to the increasing time and the semi-filled symbols represent measurements at intermediate cycles.

As can be seen in Fig. 4, a progressive decrease of the performance of the fuel cell using commercial Nafion is evident after some cycles of operation at high temperatures. Although an overall decrease of the fuel cell performance is observed, the ohmic drop overpotential seems to be the more relevant one. This behavior can be attributed to an irreversible loss of the water retention capacity, probably due to a structural degradation during operation at high temperature and reduced RH. On the other hand, the polarization response of the Nafion-$TiO_2$ hybrid was found to be highly stable, showing no evidence of degradation after 90 h of fuel cell operation at high temperatures. The data indicated that there is no significant variation of the $TiO_2$ content in the electrolyte during operation. Such a loss of the inorganic phase would be probably noticed in the ohmic drop polarization region of the curves. More important, the results displayed in the Fig. 4 revealed that the inorganic phase plays a major role regarding the structural (mechanical) stability of the hybrid electrolyte, preserving the proton conductivity after high temperature operation of the fuel cell.

## Conclusions

Summarily, Nafion-$TiO_2$ hybrids were prepared by *in-situ* sol-gel process using Ti-peroxy precursor at low temperature and the performance of PEMFC was evaluated up to 130 °C and in reduced RH. In spite of the pronounced ohmic drop displayed by the hybrid electrolytes, a significant improvement of the fuel cell performance was observed in both high temperature and reduced RH conditions when compared to unmodified Nafion. This improvement might be mainly associated with a more efficient water management due to the hygroscopic properties of the oxide nanoparticles. In contrast to unmodified Nafion, no degradation of the hybrid membranes was observed, indicating that leaching out of the inorganic phase from the membrane is absent. In addition, the presence of the inorganic phase has an important contribution to the structural resistance of Nafion, conferring to the hybrid membrane a high stability in severe fuel cell operating conditions.

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