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# An optical and single cell study of the assembly of a PEMFC with dry and expanded Nafion

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## ABSTRACT

The expansion of Nafion by water uptake poses a practical problem for the assembly of a fuel cell. In order to determine an appropriate assembling procedure, a study is presented of the expansion of a standard membrane (dispersion cast NRE-212) by water absorption under compression, and its influence on the response of a fuel cell. The expansion of uncompressed NRE-212 membranes determined by optical microscopy is 9.4% in plane and 30% in thickness, after soaking in water at room temperature. No significant difference is observed in the expansion of the membrane covered with a catalyst layer (catalyst coated membrane, CCM). Cross-sectional imaging of membrane-electrode assemblies (MEAs) shows that under compression between plates mimicking the gas flow field of a cell, the membrane undulates with micrometric amplitude ( $\sim 100 \mu\text{m}$ ), following ribs and channels of the plates, whereas the gas diffusion layer (carbon cloth) deforms and enters the channel covering 25% of its  $1 \text{ mm}^2$  section. No significant differences in the cross-section profile are observed if mounting a dry or a previously humidified, expanded, Nafion membrane, neither by submitting it to dry–humidification cycles. However, single cell response shows important differences between cells assembled with dry membranes and cells assembled with previously expanded membranes. Polarization curves show that the assembly with an expanded membrane gives rise to lower internal resistance, allowing for an improvement in the maximum power density of about 7% at  $50 \text{ }^\circ\text{C}$  and about 13% at  $80 \text{ }^\circ\text{C}$ , under standard testing conditions. Impedance spectroscopy shows that the improved response of the pre-expanded membrane must be attributed entirely to better ionic conductivity, especially noticeable when measured at high temperature ( $80 \text{ }^\circ\text{C}$ ). On the other hand, some increase in catalyst layer resistance is registered with the pre-expanded membrane that we attribute to a reduction in the catalyst surface density as a consequence of the expansion. This effect is less important than the ionic resistance effect for the response of the cell. From a practical point of view, the assembly with wet, fully expanded, membranes performs better at high current densities ( $>0.2 \text{ A cm}^{-2}$ ). At lower current densities, the assembly with a dry membrane performs like the expanded one.

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## Introduction

Water absorption by Nafion polymer membranes gives rise to expansion in the three dimensions. For a standard Nafion membrane, like the non-reinforced dispersion cast NRE-212 with an equivalent weight  $EW = 1100$ , a change from a base dry state (5% water content) to a fully humidified state (50% water content) produces an average linear expansion of 10% according to manufacturer specifications. The expansion takes place in-plane and in-thickness resulting in a total volume expansion which is usually above the nominal 37% resulting from the volumes addition of the two mixing phases ( $(V_{Nf} + V_{H_2O})/V_{Nf} = 1 + \lambda \rho_{Nf} PM_{H_2O} / (\rho_{H_2O} EW)$ , where  $V_i$  are the respective volumes of each phase,  $\rho_i$  the densities,  $PM_{H_2O}$  (=18.0) the water molecular weight, and  $\lambda$  is the number of water molecules absorbed per sulfonic group). The excess volume, 'free volume', is a function of the amount of water absorbed [1], and reflects changes in microstructure suffered by the membrane upon water absorption consisting of the rearrangement of the polymer chains forced by the interaction of water with hydrophilic groups of Nafion and its repulsion from the polytetrafluoroethylene (PTFE) matrix [2–7]. Under full hydration, grouping and reorientation of the sulfonic groups of the lateral chains give rise to hydrophilic clusters connected by channels, where liquid water is able to enter and move, providing ionic conductivity to the membrane. Such channeled microstructure allows for an appreciable ionic conductivity already at low water concentration ( $\lambda = 2$ ) [8], and in the order of  $100 \text{ mS cm}^{-1}$  when fully hydrated ( $\lambda = 22$ ) [9]. The water molecules within the membrane structure have been observed as free, loosely bound, and strongly bound molecules, according to dielectric relaxation spectroscopy measurements [10]. Similarly, lifetime decay infrared spectroscopy measurements on Nafion 117 shows changing nature of water with hydration level, from embedded water at  $\lambda = 1$ , sub-ensembles of water molecules at  $\lambda = 5$ , and bulk water at  $\lambda > 7.5$  [11]. Under current flow, a water concentration profile develops within the membrane, from  $\lambda = 4$  in the anode side to  $\lambda = 8$ – $10$  in the cathode side, according to micro-Raman spectroscopy measurements [12].

Together with the increased ionic conductivity, mechanical properties also change by water uptake. The Young modulus ( $E$ ) decreases by increasing the water volume fraction ( $\epsilon$ ) according to an empirical relation ( $E = E_0 e^{-2.17\epsilon}$ ) [13]. Satterfield and Benziger [14] found more complex dependence of Nafion tensile properties by increasing water activity; at room temperature,  $E$  registers a maximum at low water activity ( $a_w < 0.3$ ) and a decrease under full humidification; at  $90^\circ\text{C}$ , the same maximum is registered at the same water activity but  $E$  increases at full humidification. They conclude that bulk microphase ordering is concomitant with larger elastic modulus at temperatures below  $90^\circ\text{C}$ , water activity above 10%, and strain above 10%.

Nafion expansion by water uptake poses, on the other hand, a practical problem for the assembly of a fuel cell, since dimensional change may cause misalignments and the obstruction of conduits and channels for gas and water flow. This problem may be tackled by using modified Nafion membranes with a reduced expansion capability. Such membranes

are prepared from Nafion solutions containing additives, like  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{CeO}_2$ , carbon nanotubes, or imidazole, and have lower expansion by water uptake, below 5% under standard conditions, and higher capability to retain water [15]. Modified membranes are indicated for special operation conditions, such as low relative humidity and high cell temperature, above  $90^\circ\text{C}$ , with hydrogen as fuel. At lower temperature and high humidification conditions their use is less appropriate, because the conductivity drops below that of pure Nafion, and they may favor flooding of the electrodes due to their high water retention. Modified membranes are at present a matter of intense research in aspects like the interaction of the filler with the polymer matrix, their compatibility with the catalyst, fuel cross over rate, and durability.

When the use of Nafion membranes without modifiers is required, their expansion by water uptake must be taken into account for the assembly of the cell. Two assembly procedures may be considered in this respect. One is the assembly with a membrane fully humidified and brought to expanded dimensions. This procedure poses certain practical difficulties, like handling humidified membranes, controlling ambient humidity, and may be difficult to integrate in a process chain. Humidification may also result in the detachment and loss of catalyst layer when carried out on catalyst-coated membranes (CCMs). A second possibility is the assembly of the cell with a dry membrane. In this case, the assembly procedure is easier and may be incorporated with less difficulty in chain processes; however since the membrane is first compressed by the flow-field plates and then humidified, water absorption occurs under constrained conditions by the flow field plates and the electrodes. Membranes humidified under compression have different properties than the uncompressed humidified ones and may change fuel cell response.

Membrane properties are affected by compression because water uptake capability and viscoelastic properties depend on compression [16–19]. When compressed by the fuel cell flow field, membrane swells more in the channels than in the ribs regions, and total water uptake diminishes by about 14% according to in situ measurements by Lai et al. [18]. Electrodes on both sides of the membrane induce additional lateral confinement altering further water absorption and expansion behavior [18,20]. Mechanical damage of the membrane by pinholes formation may also be enhanced by the expansion properties of Nafion, shortening its durability [21].

Therefore, the assembly of a fuel cell with dry or expanded membrane must be decided in view of practical aspects related with the assembly procedure, and the impact on the fuel cell response. To our knowledge, there is no previous analysis of this subject in the literature, in particular of the impact of the membrane assembly procedure on the fuel cell response.

In this work, a comparative study is carried out of the membrane assembly procedure on the response of proton exchange membrane fuel cell (PEMFC). With this aim, the study comprises firstly the analysis of membrane expansion upon water uptake and under compression mimicking the real situation in a fuel cell. In a second part, performances of single cells are compared with the membrane installed in dry form and in fully humidified-expanded form, using polarization curves and impedance spectroscopy.

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