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Operando μ-Raman study of the actual water content of perfluorosulfonic acid membranes in the fuel cell

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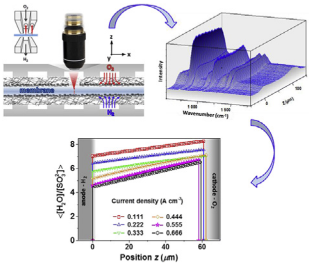
HIGHLIGHTS

- *Operando* μ-Raman is used to probe water across the membrane during operation.
- Different relative humidity, stoichiometry and current conditions are studied.
- The hydration behaviors of Nafion® N115 and Aquivion™ E790-05s are compared.
- Both membranes loose water with the increase of current density.
- Thermal management is the main reason of the membrane dehydration.

GRAPHICAL ABSTRACT



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ABSTRACT

Operando μ-Raman spectroscopy is used to probe the water distribution across Nafion® and Aquivion™ membranes in the operating fuel cell. The through-plane water concentration profile is obtained with μm resolution at the middle of the active surface, both at the gas distribution channel and at the under-lands areas. Depth-resolved measurements carried out at room temperature show that the water content of both membranes increases with the increase of the feed gas relative humidity and decreases with the increase of stoichiometry. At given relative humidity and stoichiometry conditions, the water content first increases at the fuel cell start-up and, then, decreases progressively with the increase of the current density delivered by the cell. The water loss is due to the concomitant rise of pressure drops and of the cell inner temperature, the latter giving the larger contribution. Pressure drops are related to the increase of the feed gases fluxes while temperature rise is due to increasing ohmic losses and heat from the electrochemical reaction. Compared to Nafion, Aquivion exhibits larger water content, but similar dehydration rate as a function of ohmic losses, and larger water accumulation at the under-lands area compared to channel.

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1. Introduction

Hydrogen-fuelled Proton Exchange Membrane Fuel Cells (PEMFCs) are considered as promising clean power sources for portable, mobile and stationary applications. Although this technology has been at the forefront of commercialization efforts in the last two decades, especially by automakers, breakthroughs are still needed to fulfil all cost and durability specifications [1].

The PEMFC operation involves a number of chemical and physical phenomena, as electrochemical reactions, heat, mass and charge transfers. All these phenomena are strongly related to the water content and distribution throughout the FC core, *i.e.* the membrane-electrodes assembly (MEA), and the membrane hydration plays a key role. On the one hand, proton transport resistance of the membrane represents a main contribution to the ohmic losses and related Joule heating affecting the FC performances at high currents [2]. But adequate proton conductivity can only be achieved at the hydrated state of the state-of-art membranes *i.e.* the perfluorosulfonic acid (PFSA) ionomers [3,4]. On the other hand, excess water vapour pressure in the MEA induces condensation (usually referred to as “flooding” phenomenon) that prevents the effective access of reactants to the catalyst sites [5]. Also, cell operation under flooding over a long time increases corrosion of the different MEA components, including catalyst particles dissolution into the membrane [6]. Contrarily, long operation under dry conditions usually causes the mechanical and chemical degradation of the membrane [6]. The water management issue is, then, the need to maintaining the proper membrane hydration without causing electrode flooding. The effective management of water in PEMFCs, being essential for both high performances and durability, represents a key challenges for the significant improvement of this technology in the next future [2,6–8].

PEMFCs exhibit layered structure, with separation of the energy converter and the energy storage and the presence of different porous media. This spatial heterogeneity implies inhomogeneous through-plane and in-plane conditions concerning the concentration of reactants and water as well as pressure and temperature. Reactants are progressively converted into products from the gas inlet to the outlet. Simultaneously, the produced water is redistributed between anode and cathode by interrelated charge and mass (H^+ and H_2O) transport processes through the membrane thickness. The combined effect of the whole phenomena is the fully 3D water distribution throughout the cell. Additional complexity arises from the fact that: (i) the water transport properties of the membrane, *i.e.* water diffusion and electroosmotic coefficients, depend in turn on the membrane water content. (ii) Through-plane water fluxes are presumably affected by the in-plane variation from channel to lands, because of the different local constraints to the porosity of the active (AL) and gas diffusion layers (GDL) and to the membrane swelling. The consequence of the heterogeneous water distribution is the heterogeneity in the way the FC performs and degrades.

The accurate prediction of the actual water distribution through the different MEA components is a difficult task owing to the complex back-coupling between a huge number of parameters as the macroscopic operating conditions, the FC components design, the local environmental conditions, the dominant transport mechanisms and the ageing effects. It should then be pointed out that usual characterization methods as external water balance and cell potential/resistance monitoring are integral measurements averaging on the whole active surface, whose results can be crude when looking for accurate and effective water management strategies. Thus, a consequent research effort has been performed over the past decades on the development of *operando* techniques able to probe the local water content in the different MEA components, more particularly within the membrane [9]. Non-intrusive techniques such as proton nuclear resonance imaging (MRI) [10–19], neutron [20–23] and X-ray [24–27] absorption and small angle neutron scattering (SANS) [28–34] have been more widely investigated but their use stays hindered by their specific requirements, *e.g.* the need to avoid magnetic components for the FC fixture in MRI, too low resolution for the neutron/X-ray absorption, and limited access to neutron beam for the SANS measurements [9]. Only recently, confocal Raman microspectroscopy has emerged as an alternative method for the local water detection across the membrane in the working FC [35–39]. μ-Raman is a laboratory-scale technique with the ability to give the absolute amount of sorbed water with both in- and through-plane μm spatial resolution [40]. Raman spectra are collected at increasing depth along the membrane thickness. After correction of the raw signal, the amount of sorbed water is calculated for each probed position using the intensity of the corresponding vibrational bands. The reader is referred to [40] for details of water depth-profiling across perfluorosulfonic polymers.

In a previous article, we reported *operando* μ-Raman measurements across bi-layer membranes made of Nafion® and Aquivion™ with different side chain length and equivalent weights, stacked together [39]. Results showed that the orientation of the equivalent weight gradient with respect to the proton flow and the water external activity affects the membrane water content, the related water transport ability and, thus, the water distribution through the MEA and the FC operation. However, the membrane hydration was probed only at a limited area in front of the gas distribution channel. The present work intends to improve the understanding of relationships between the FC operating conditions and the membrane water content and distribution by studying Nafion® and Aquivion™ separately. First, our study focus on the most commonly used Nafion® N115, one of the benchmark long-side-chain (LSC) materials for PEMFCs. Then, the Nafion® hydration behavior is compared to that of Aquiviont™ E79-05s, which belongs to advanced short-side-chain (SSC) membranes for which superior performances have been reported (see Refs. [41,42] and references therein). The water distribution across the membrane thickness is probed at the middle of the active area, at the feed gas distribution channel and under the lands for current collection. The effect on the membrane hydration of different FC operating conditions of current density, relative humidity (RH) and feed gases stoichiometry (*i.e.* flow rate) is investigated. Results obtained with the FC operated at T_{room} and whose temperature is not managed emphasize the concern of the coupled thermal/water management issue.

2. Experimental

2.1. Cell

Fig. 1 shows the PEMFC for *operando* μ-Raman measurements. Stainless steel monopolar plates with single serpentine gas distribution channel (active area of 9 cm^2) are coated by a 10 μm thick gold layer to avoid corrosion which could degrade the current collector/GDL interface. The depths of the channels are 0.5 and 1.5 mm for the upper (cathode) and lower (anode) plates respectively. The width of channel and lands is 1.5 mm at both sides. The upper gas distribution plate is modified as to accommodate the microscope objective and a ⌀1.2 mm hole is drilled in the middle of the active area, either at the gas distribution channel or at the land for the current collection. This viewing aperture provides the optical path for the Raman exciting radiation to the membrane. The airtightness of the cell during μ-Raman measurements is ensured by a compressible gasket squeezed by the Raman objective.