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In situ analysis of water management in operating fuel cells by confocal Raman spectroscopy

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ABSTRACT

A fuel cell has been specially designed for the study of the water management in situ and operando by confocal micro-Raman spectroscopy. Water concentration profiles across the working Nafion® membrane have been extracted for different operating conditions. The characterisations performed in front of the gas distribution channel show an extreme sensitivity of the membrane water content to the local relative humidity. Electrochemical impedance spectroscopy measurements, carried out in parallel, reveal that these averaged values can be misleading when used to obtain information on the local membrane hydration state.

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1. Introduction

The understanding of water management in operating proton exchange membrane fuel cells (PEMFC) is a major issue for the development of this technology. The complex interplay of a range of transport and electrochemical processes occurring in the heart of the system leads to spatial heterogeneity in water repartition and, as a consequence, in the way that PEMFC performs and degrades.

PEMFC performances strongly depend on the hydration state of the polymeric electrolyte. Thus, lots of efforts have been devoted to the quantitative measurement of the membrane heterogeneous water content using sophisticated techniques. Neutron absorption [1–5] and NMR imaging [6–9] give effective information about the in plane local distribution of liquid water. However, these techniques suffer from the ability to resolve the membrane swelling. So, even if the potential for higher resolution exists [10], the spatial resolution currently reported for experiments carried out on working FCs (20–50 μm) prevents the determination of the water concentration gradients across 25–50 μm thick state-of-art membranes. X-ray diffraction is a very promising, emerging method which allows scanning the membrane thickness in real time, down to a few micrometers of spatial resolution [11]. But the sample has to be spread out with very high energy (synchrotron) radiation and the experimental set up implies no spatial resolution at all along the X-ray beam path. Up to date, the most efficient method appears to be small-angle neutron scattering [12–14] because a cell transparent to neutrons can be built without any local perturbation of the FC operation. However, the use of this technique is up to now restricted to the study of perfluorinated ionomer membranes because of the need of high contrast values and the easily interpretable evolution of the scattering spectra upon swelling. It is therefore very appealing to develop an efficient laboratory technique that could be used with a wide range of membranes, for the determination of the water management in operating FCs representatives of state-of-art in terms of geometry and performances.

Confocal Raman spectroscopy has been recently employed to determine the concentration profile of water and methanol diffusing through the Nafion® membrane thickness, during permeation experiments [15–17]. Also, H. Matic et al. reported in situ micro-Raman measurements of water distribution inside Nafion® in an operating H_2/H_2 electrochemical cell [18]. All these pioneering works, even if carried out under highly idealized experimental conditions as compared to the real fuel cell environment, show the great potential of this technique i.e. direct dependence of the Raman signal on the quantity of interest and spatial resolution on the level of micrometers.

This paper deals with the design of a new H_2/O_2 PEMFC allowing the analysis of the water distribution across the membrane thickness by confocal Raman spectroscopy. First results obtained in the centre of the active area, as a function of the FC operating conditions, are presented.

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2. Experimental

A specific 9 cm^2 FC test fixture has been designed and built for Raman analysis, so that the surface of the membrane is perpendicular to the laser beam optical axis (Fig. 1). The cell is made of two 20 mm thick gilded stainless steal monopolar plates with a single machined serpentine gas distribution channel. Plates are used as current collectors, end plates and of course as reactants distributors. The depths of the channels are 0.5 and 1.5 mm for the upper (cathode) and lower (anode) plates respectively. The width of the ribs and channels are the same for both plates, i.e. 1.5 mm. A 1.2 mm hole is drilled in the channel in the middle of the active area of the upper gas distribution plate. This hole is enlarged on the external side of the plate (Fig. 1a) so as to be adapted to the shape of the microscope objective and to allow the displacement of the focalisation point at variable depth across the membrane thickness. A highly compressible gasket, squeezed by the Raman objective, is used to keep the cell tight, especially during scanning through the thickness.

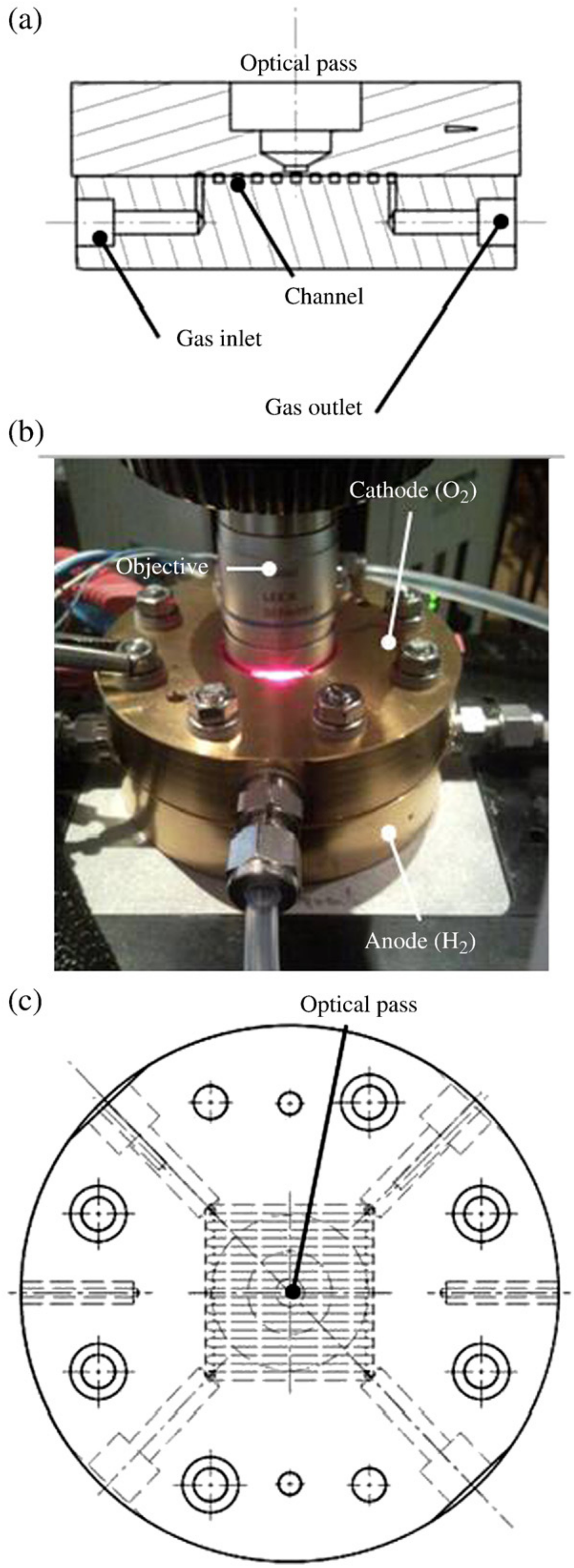

Fig. 1. Schemes and picture of the PEMFC for in situ Raman analysis: (a) cross-section, (b) during experiment and (c) top view.

Nafion® N115 membranes are purchased from DuPont and used as received. The membrane is stacked directly into the cell, between two commercial electrodes: Johnson Matthey on Toray paper TGP-H-060 (0.4 mg cm^{-2} Pt). Catalyst coated backing are glued on the gas distribution plates and a 400 µm diameter hole is drilled in each of them. Then, the cell is stacked with the membrane and put into oven at 135 °C to stick the membrane onto the electrodes.

It should be mentioned that, under the experimental conditions applied in this work, the local removal of the active and gas diffusion layers is considered to have neglible impact on the water flow across the membrane thickness in the probed area. As far as the membrane segment located in the gas distribution channel is concerned, the water diffusion coefficients trough the active and gas diffusion layers are known to be larger than that through the polymer electrolyte. Also, the amount of water produced by the active layer in the area corresponding to the 400 µm hole (~10^{-9} mol s^{-1} at 222 mA cm^{-2}) is considerably lower than the water amount driven by the humidified gas (~10^{-5} mol s^{-1}) and so no significant variation of the local RH is expected.

Raman spectra are obtained by excitation with 647.1 nm radiation from an Ar–Kr laser operating at about 100 mW. The spectra are recorded with a LABRAM1B confocal Raman spectrometer (Jobin–Yvon S.A., Horiba, France), equipped with a 50X Leica objective (HCX PL Fluotar L 50X/0.55, working distance 8 mm) recovering the backscattered light. Heater mats are used to keeping the objective at 38 °C and avoid water condensation on the lens during FC operation. The FC is mounted on an automatic positioning device that allows carrying out spectral measurements transversally, at different depths across the membrane cross section. Typically, a set of ~100 Raman spectra is collected through the upper channel/membrane/lower channel system with a scan step of 2 µm. The total time required for a complete scan is ~15 min. The in-depth resolution of the objective, as estimated under the applied experimental conditions, is 7 ± 1 µm.

The single cell test fixture is operated using a Biologic FCT 50S test bench for cell temperature, gas flows and pressures regulations. A Biologic potentiostat/galvanostat/impedancemetre VSP (with VMP 2B booster) is used for the cell current/voltage management and in situ electrochemical impedance spectroscopy (EIS) measurements. The gas inlets relative humidities (RH) are controlled with bubble chambers and measured at the outlets with a Rotronic HygroPalm capacitive sensor. Electrochemical tests are performed in counter-flow configuration, under pure hydrogen and oxygen at 1.1 bars, at variable gas flows, RH and temperature.

In order to evaluate water content under dynamic equilibrium conditions for water transport, the FC is operated during at least 4 h before Raman acquisition, up to attain steady electrochemical performances. Three scans are carried out for each experiment. No changes of the FC ohmic resistance occur during the time needed.

3. Results and discussion

Fig. 2 compares typical Raman spectra of Nafion® N115 membrane at various hydration states. Both the signals arising from the fluorinated matrix (ν_sC-F mode at 725 cm^{-1}) and the water molecules (νO–H band around 3450 cm^{-1}) are clearly visible and separated. Being the Raman

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