



Short communication

A novel (*ex situ*) method to quantify oxygen diffusion coefficient of polymer fuel cells backing and catalyst layers



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HIGHLIGHTS

- Knudsen radius and effective diffusivity are measured for porous layers of HT-PEMFC.
- Knudsen diffusion is 30% and 50% of transport resistance of MPL and CL.
- High temperature PEMFC porous media can be treated as isobaric.
- Characterization of support layer is important to further improve uncertainty.

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ABSTRACT

Limiting current density of oxygen reduction reaction in polymer electrolyte fuel cells is determined by several mass transport resistances that lower the concentration of oxygen on the catalyst active site. Among them, diffusion across porous media plays a significant role. Despite the extensive experimental activity documented in PEMFC literature, only few efforts have been dedicated to the measurement of the effective transport properties in porous layers. In the present work, a methodology for *ex situ* measurement of the effective diffusion coefficient and Knudsen radius of porous layers for polymer electrolyte fuel cells (gas diffusion layer, micro porous layer and catalyst layer) is described and applied to high temperature polymer fuel cells State of Art materials. Regression of the measured quantities by means of a quasi 2D physical model is performed to quantify the Knudsen effect, which is reported to account, respectively, for 30% and 50% of the mass transport resistance in micro porous layer and catalyst layer. On the other side, the model reveals that pressure gradient consequent to permeation in porous layers of high temperature polymer fuel cells has a negligible effect on oxygen concentration in relevant operating conditions.

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1. Introduction

Maximum power density of polymer electrolyte membrane fuel cells (PEMFC) is limited, in most relevant cases, by the availability of oxygen on the catalyst active sites. Several contributions are known in the literature to be responsible for oxygen transport limitations and the most relevant ones are [1]: laminar convection in the distributor, diffusion in the porous layers and, ultimately, the resistance to oxygen transport in the electrolyte thin film. The separation and quantification of each contribution is a complex task that must be carried out by combining *in situ* and *ex situ* techniques. For this reason, *ex situ* characterization of mass

transport properties of backing layers has been performed extensively in the low temperature PEMFC literature, here briefly reviewed.

J. T. Gostick [2] analyzed the permeability of commercial backing layers focusing on in-plane and through-plane permeability, the effect of porosity, PTFE content and compression. L. M. Pant [3] extended the previous study to the analysis of the micro porous layer (MPL) and estimated the Knudsen contribution to the transport resistance by changing the permeating gas.

U. Beuscher [4] estimated the diffusion coefficient of the backing layer with *in situ* limiting current measurement technique. The author concluded that the sum of channel and porous media resistances constitutes approximately 50% of the resistance measured in mass transport limited regime; the remaining resistance was attributed to Knudsen diffusion and liquid water/ionomer thin film diffusion.

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R. Fluckinger [5] studied anisotropy of gas diffusion layers (GDL) with diffusimetry; this technique, that takes advantage of the existing analogy between Ohm's law and Fick's law, consists in soaking the porous sample with liquid electrolyte and performing electrochemical impedance spectroscopy.

A. Casalegno [6,7] and J. La Manna [8] characterized water transport in PEMFC porous media by flowing humid and dry air streams at opposite sides of a planar GDL sample; the measurement of relative humidity at the outlet was the tool that allowed the authors to analyze water flooding and separate GDL and MPL transport resistances.

N. Zamel [9] and C. Chan [10] adapted a Lochschmidt cell to characterize PEMFC porous media. Mass transport properties are regressed by fitting the experimental data with the analytical solution for monodimensional transient diffusion in a stagnant medium.

A recent study by S. Litster [11] reported an application of nano scale computed tomography to the analysis of the catalyst layer microstructure and, in combination with a model, the authors estimated the effective transport properties, *i.e.* Knudsen radius and effective diffusion coefficient.

High temperature PEMFC [12] share the same backing layer materials available for low temperature PEMFC with similar CL structure, thickness and properties, but, to the authors' knowledge, works characterizing accurately mass transport properties of these components are not available in the literature, even though mitigation of the mass transport resistance is of crucial importance. The presence of liquid phosphoric acid is reported to generate additional mass transport resistance in the catalyst layer by obstructing the pores available for gas diffusion [13,14].

In the present work a methodology for *ex situ* characterization of mass transfer properties of GDL, MPL and CL is described and applied to state of art materials for high temperature PEMFC. The experiment consists in flowing air and nitrogen at opposite sides of a planar porous sample in order to induce steady state diffusion of oxygen and nitrogen across. By measuring the oxygen mole fraction and total molar flow rate at the outlet, the effective diffusion coefficient and Knudsen equivalent radius of each sample are fitted on the experimental data with a physical based literature model. The improvement achieved with the methodology presented in this work, in comparison with the relevant literature, consists in the possibility to apply accurate measurement techniques to assess the oxygen content in the stream, *i.e.* gas chromatography.

2. Experimental

2.1. Experimental setup

A sketch of the experimental setup is presented in Fig. 1(a). The porous sample is placed into a specific hardware composed by two graphite triple-serpentine distributors (Fuel Cell Technology Inc.) and aluminum end plates compressed by 8 bolts at 12 Nm torque. The distributors are divided into a pre-heating section, which guarantees constant temperature of the flowing gas, and an active section, where mass transfer across the porous sample takes place. A PTFE window gasket is used to avoid external and internal gas leakage.

Standard air and nitrogen flows (99.9999% purity) are enabled at the opposite sides of the porous sample and controlled by two flow meters (uncertainty 0.7% of the setpoint plus $0.004 \text{ NI min}^{-1}$). Four absolute pressure transducers (uncertainty 100 Pa) are positioned at the sample inlets and outlets, while two differential pressure transducers (uncertainty 30 Pa) measure the pressure difference across the porous sample at the inlet and at the outlet of the active zone. Two needle valves are manually regulated in order to manage the gas pressure, according to the testing conditions and the

specific experiment. At the air outlet oxygen and nitrogen mole fractions are measured with a μ -gas chromatograph, which has been calibrated at the beginning of the experimental activity at four oxygen concentration levels between 20.9% and 5%. The combined relative uncertainty is estimated in 1% of the reading with 95% confidence. In addition, a calibrated flow meter (uncertainty 0.7% of rate plus $0.004 \text{ NI min}^{-1}$) measures the gas flow at the air outlet. The temperature of the sample holder is measured by two thermocouples (type K).

2.2. Experimental methodology

The characterization of porous layers consists in two consecutive experiments. It is referred to the first one as the *diffusion test* (or balanced-pressure experiment), while to the second one as the *permeation test* (or balanced-concentration experiment).

In the *diffusion test*, the pressure difference across the sample is minimized. In order to set zero differential pressure both at inlet and outlet, two experimental parameters are controlled: the manual needle valve at the outlet and the air flow rate (regulated by digital flow meter/controller). This is achieved by applying the following experimental protocol (detailed operating conditions reported as [Supplementary materials](#)):

1. Nitrogen flow is enabled and set accordingly to the testing conditions; a needle valve at the nitrogen outlet is regulated to maintain the absolute pressure required by the test;
2. Air flow is enabled and set to a guess value; a needle valve at the air outlet is regulated to maintain the absolute pressure required by the test;
3. Air flow and outlet needle valves are finely regulated until a steady and zero pressure difference is measured across the sample at both the inlet and outlet. Because of fluctuation of testing conditions, the pressure difference is never zero, but after equilibration (steps 1–3), it is less than measurement uncertainty;
4. Oxygen concentration and flow measurements are recorded. Final values are computed by averaging values obtained in 10 min operation.

The described procedure is repeated at increasing nitrogen flow rates, according to the testing conditions reported in [Supplementary materials](#).

In the *diffusion test*, unbalanced differential pressure across the sample results in bulk flow (or convective flow) through the porous layer, affecting the measurement since it is erroneously attributed to diffusion. Bulk flow is a problem that affects the characterization of GDL only, while it has negligible effect for samples with MPL or CL (as also discussed by Lamanna [8] and Casalegno [6]). Convection through GDL results in non-equimolar mass transfer across the sample. To check equimolarity, the authors included, in the experimental setup, a measurement of gas flow rate at the outlet, which allows to verify consistency between inlet and outlet flow rates.

After the *diffusion test*, the *permeation test* is carried out on each sample, according to the following protocol:

1. Air flow is disabled while the nitrogen flow is set according to the condition of the test;
2. A needle valve at the air (nitrogen) outlet is set open (closed);
3. The pressure difference across the sample is recorded and averaged over 5 min.

The described procedure is repeated for increasing nitrogen flow rates, sequentially 0.2, 0.4, 0.6 and 0.8 NI min^{-1} .

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