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In operando measurements of liquid water saturation distributions and effective diffusivities of polymer electrolyte membrane fuel cell gas diffusion layers

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ABSTRACT

In this work, the *in operando* determinations of liquid water saturation and corresponding effective diffusivities were measured for polymer electrolyte membrane fuel cell gas diffusion layers (GDLs). Through-plane liquid water saturation profiles were obtained by combining liquid water thicknesses measured from *in operando* synchrotron X-ray radiography and the GDL porosity distributions from ex situ X-ray computed tomography. The effective diffusivity of these partially saturated GDLs were determined from electrochemical impedance spectroscopy (EIS) measurements combined with results from our one-dimensional fuel cell impedance model. The ratio of the effective diffusivity of the GDL to the oxygen bulk diffusivity was found to follow a power law relationship, $(1-s_{avg})^{2.80}$ which is in agreement with measurements typically reported in the literature from limiting current and three-dimensional mass transport models. The methodology presented in this paper provides a novel, *in operando* and complementary alternative technique for measuring the effective diffusivity of partially saturated GDLs.

1. Introduction

Operating at high current density is a promising strategy for improving the power density, compactness, and overall cost competitiveness of polymer electrolyte membrane fuel cells (PEMFCs) [1]. Under high current density operation, the effective management of mass transport phenomena is critical for improving fuel cell performance [2,3]. The gas diffusion layer (GDL) is a key component of the PEMFC that must facilitate the transport of: reactants (oxygen and hydrogen) from the gas channels to the catalyst layers (CLs), excess liquid water to the gas channels, and electrons and heat between the flow fields and the CLs [4]. The GDL, also known as the porous transport layer (PTL) or gas diffusion medium (DM), typically consists of two porous layers: the microporous layer (MPL) and the carbon paper substrate. In designing the GDL, the needs of competing phenomena must be delicately balanced. For example, smaller pores may be attractive for their higher liquid water entry threshold capillary pressures, which can lead to lower liquid water saturations [5,6]; however, these small pores can restrict the diffusivity of reactant gases within the GDL. Further insights are required to prescribe optimal micro- and nano-scale structures of the GDL, and in particular a quantitative relationship between the gas transport properties and the liquid water content of the GDL is needed to inform new GDL designs for improved fuel cell performance [2,7,8].

The effective diffusivity of the GDL is an important parameter used to measure how quickly gaseous fuels can travel through the porous medium to support the electrochemical reactions that drive the fuel cell. In partially-saturated GDLs, the effective diffusivity is commonly written with respect to the material porosity (ε) and liquid water saturation (s) as follows:

$$\frac{D_{eff}}{D_{bulk}} = f(\varepsilon)\cdot g(s), \tag{1}$$

where D_{eff} and D_{bulk} are the effective and bulk diffusivity coefficients, respectively. The functions, $f(\varepsilon)$ and $g(s)$, are usually

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Nomenclature

Parameters and variables

b	Tafel's slope (V)
c_{tot}	Air molar concentration
c^{ref}	Oxygen molar concentration in the channel (mol/m^3)
C_{DL}	Double layer capacity (F/m^2)
D	Oxygen diffusivity of domain (m^2/s)
E	Voltage (V)
E^{ref}	Fuel cell reference potential (V)
F	Faraday constant (C/mol)
f	Function characterizing the effect of the structure
g	Function characterizing the effect of the saturation
i	Complex unity
i_0	Cathodic exchange current (A/m^2)
I_{cell}	Fuel cell current density (A/m^2)
J	Cost criterion
L	Length (m)
n	Exponent
N	Molar flux (mol/s)
P	Total air pressure (Pa)
P_{O_2}	Oxygen partial pressure (Pa)
R	Ideal gas constant (J/mol/K)
R_Ω	Ohmic resistance (Ω)
s	Liquid water saturation
SV	Number of solid voxels
t	Time (s)
T	Temperature (K)
VV	Number of void voxels
x	Oxygen mole fraction of domain
X_w	Water thickness (cm)
y	Through-plane coordinate (m)
z	In-plane coordinate (m)
Z	Complex impedance (Ω cm^2)
δ	Complex notation
ε	Porosity
ε_{VF}	Void fraction
η	Voltage loss in the domain k (V)
μ	Water absorption coefficient (cm^{-1})
σ	Electrical conductivity of the domain k (S/m)
ω	Angular frequency (rad/s)

Superscripts and Subscripts

avg	Average
bulk	Bulk
cell	Fuel cell
C	Catalyst layer
CP	Carbon paper
eff	Effective
exp	Experimental
GDL	GDL
in	Inlet
M	Membrane
MPL	MPL
N_2	Nitrogen
out	Outlet
O_2	Oxygen
ref	Reference

expressed as power law relationships, i.e. ε^n and $(1-s)^m$. Exponential values n and m reported in the literature are typically determined numerically, based on an analytical approach [9] or 3-dimensional (3D) mass transport modeling, such as lattice Boltzmann Method (LBM) [10–13], pore network modeling [14,15] and computational fluid dynamics [16]. However, in order to determine the effective diffusivity of materials *in operando*, experimental methods are required. Several authors reported the measurement of effective diffusivities of dry [17,18] and partially saturated GDLs [19] using the limiting current technique. This is a valuable technique, but a delicate experimental protocol is required whereby limiting currents are measured for a range of oxygen concentrations and operating pressures. Alternative methods for measuring the effective diffusivity of the GDL would be highly valuable [7].

Electrochemical impedance spectroscopy (EIS) is one of the most promising candidates for providing in situ GDL effective diffusivity measurements [20]. Using this technique, fuel cell properties, including the GDL mass transport resistance [20,21], can be measured in an operating fuel cell under a wide range of operating conditions (gas humidity, fuel cell current, etc.). With EIS, the mass transport resistance is usually obtained with an equivalent electrical circuit used to analyze the fuel cell impedance [21]. However, this approach cannot be used to determine the GDL effective diffusivity, and fuel cell modelling, such as one-dimensional (1D) fuel cell impedance modelling [22–26], is required. By using this modeling technique and EIS measurements at low current densities, Kulikovsky measured the fuel cell catalyst layer diffusivity [27]. By following the same methodology, GDL effective diffusivities can be determined based on EIS measurements—a valuable alternative to the limiting current technique.

In the literature, the measurement of liquid water saturation has been performed using various experimental techniques [10,19,28]. Synchrotron-based X-ray tomography can be used to directly measure the liquid water saturation in an operating fuel cell [10,29], but this imaging technique typically involves a highly specialized fuel cell design [29] as well as high beam energies, which could lead to irreversible membrane damage [30,31]. Alternatively, synchrotron X-ray radiography is a powerful method for studying fuel cell liquid water transport behaviour at spatial resolutions between 2–10 μm [32–37], and it requires lower beam intensities and minimal fuel cell design alterations. In Antonacci et al. [38,39], synchrotron X-ray radiography was successfully combined with EIS to assess the fuel cell performance for a range of GDL liquid water quantities. While liquid water saturation is not a direct output of X-ray radiography, the saturation can be determined by combining GDL porosity information.

In this work, the *in operando* determinations of liquid water saturation and corresponding effective diffusivities were measured for PEMFC GDLs. Liquid water thicknesses were measured via synchrotron X-ray radiography, and the corresponding GDL saturation values were determined through the direct comparison of GDL porosity distributions obtained ex-situ from X-ray computed tomography. The effective diffusivities for these partially saturated GDLs were determined using EIS measurements in combination with a 1D fuel cell impedance model, and the presented relationship between the effective diffusivity and liquid water saturation was in good agreement with other established techniques, such as limiting current [40] and 3D modelling with LBM [10].

2. Experimental

In this section, the techniques employed to measure the liquid water saturation in the GDL are presented. The characterization of the GDL diffusivities (D^{eff}_{MPL} and D^{eff}_{CP}) using EIS measurements combined with a 1D fuel cell impedance model are also described.