



Microscale measurements of oxygen concentration across the thickness of diffusion media in operating polymer electrolyte fuel cells



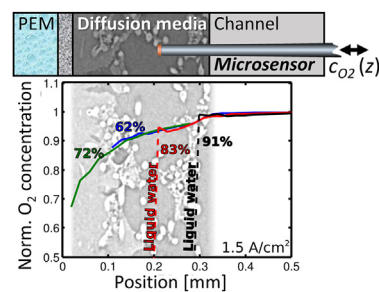
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HIGHLIGHTS

- Oxygen concentration measurements in polymer electrolyte fuel cell diffusion media.
- Measured in pores during fuel cell operation using 25 μm microsensor probe.
- Spatial resolution of 20 μm through the thickness of diffusion media.
- Spatially-correlated to structure imaged by micro X-ray computed tomography.
- Local O_2 transport resistance and liquid water onset locations in diffusion media.

GRAPHICAL ABSTRACT



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ABSTRACT

Although polymer electrolyte fuel cells (PEFCs) offer promise as efficient, low emission power sources, the large amount of platinum catalyst used for the cathode's oxygen reduction (ORR) results in high costs. One approach to using less Pt is to increase the oxygen concentration at the catalyst by reducing the oxygen transport resistances. An important resistance is that of the diffusion media (DM). The DM are highly heterogeneous porous carbon fiber substrates with a graded composition of additives across their thickness. In this work we use an oxygen microsensor with a micro-positioning system to measure the oxygen concentration and presence of liquid water in the pores at discrete points across the thickness of a commercial carbon felt DM in operating PEFCs. Under conditions with no liquid water, the DM accounts for 60% of the oxygen depletion, with 60–70% of that depletion being due to the thin microporous layer (MPL) on the catalyst layer (CL) side. Using concentration gradient data, we quantify the non-uniform local transport resistance across the DM and relate it to high resolution 3D X-ray computed tomography of the same DM.

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1. Introduction

Polymer electrolyte fuel cell (PEFC) systems have to the

potential to displace combustion engines and batteries in a wide range of transportation, portable, and stationary power applications because of their high efficiency, power and energy density, and zero exhaust carbon emissions. Despite significant reductions in estimated costs over the past decade, projected mass produced automotive PEFC costs are still twice the desired goal [1,2]. A key contributor to that cost is the raw material cost of the

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Pt catalyst in the cathode. Despite the notable promise of new low and zero Pt-group metal catalysts [3,4], engineering to enhance the oxygen transport efficacy and increase oxygen activity at the catalyst remains a valuable pathway to retaining cathode performance while reducing Pt loading. The O₂ transport resistances include those through the flow field [5,6], DM [7–9], the CL [10–12], catalyst agglomerate [13,14], polymer electrolyte films [12,15–17], and component interfaces [18,19]. Unfortunately, due to the enclosed design of PEFCs and the associated micro/nano length scales of these layers and interfaces, determining a direct breakdown of how each resistance and each feature contributes to the overall transport loss remains a significant challenge.

Our focus herein is the oxygen transport resistances specific to the DM and its spatially distinct internal features. The DM is also often referred to as the gas diffusion layer (GDL) or porous transport layer (PTL) [20]. It is typically a porous carbon layer placed between the CLs and the solid gas distribution plates (i.e., bipolar plates in a PEFC stack). It serves to distribute gases and electrical current over the entire area of the CL as well as provide mechanical support to the delicate polymer membrane. Since PEFCs are low temperature fuel cells, they can accumulate liquid product water that can additionally impede oxygen transport. To repel liquid water and maintain gas pathways, the fiber substrate is often coated with hydrophobic polytetrafluoroethylene (PTFE). A microporous layer (MPL) of carbon black and PTFE is commonly applied to the fiber substrate to improve contact with the CL [19,21].

There are a number of ways to characterize oxygen transport losses using global, cell-level measurements, largely focusing on the effect of different operating conditions and electrode compositions on PEFC performance. In-depth analysis of a PEFC's I–V curve, coupled with testing the effects of different gas mixtures, can yield insight into which mechanisms of voltage loss are dominant [22–25]. This distinction includes relative weighting of oxygen transport losses due to Knudsen diffusion in the CL pores or dissolved oxygen diffusion in the ionomer binder versus that of molecular diffusion in the DM [23,24]. In a related but more specific method, researchers also study the effect of different operating conditions on the PEFC's limiting current in order to extract cathode transport parameters and identify the dominant loss mechanisms [17,23,24,26–32]. Most recently, limiting current studies in PEFCs with carefully varied platinum loadings and feed gas conditions have yielded insight into the oxygen transport resistance local to the catalyst [28–31].

A number of modeling [33–37] and experimental [7,38–41] works have studied the interplay between water and oxygen transport in the DM. Imaging studies using synchrotron x-ray imaging [38,39] and neutron radiography [41] have demonstrated that there is significant liquid water throughout the DM in a variety of conditions. Experiments [7,39,40] and pore-network DM modeling [36,37] suggest that water forms breakthrough pathways or “capillary fingers.” As more water is generated, it tends to travel through these established finger-like pathways – rather than forming a new path. Owejan et al. [42] showed that in the absence of MPL cracks, liquid water cannot penetrate the hydrophobic MPL and water is restricted to vapor phase transport. Similarly, Zenyuk et al. [43] showed that introducing large openings in the MPL can enhance liquid water removal from the CL.

Outside of actual operating PEFCs, several studies have made *ex-situ* and computational determinations of the oxygen diffusivity of DMs [44–47] providing valuable input to DM and design and parameters for cell-scale models (computational, analytical, and theoretical). Unfortunately, the prior *ex-situ* characterizations only yield the effective properties of the complete layer and do not

resolve the local impact of morphological heterogeneity [45]. While computational characterizations of pore-scale transport in reconstructed volume offer significant spatial detail, they often lack important physics such as Knudsen diffusion and liquid water saturation [48]. In addition, spatially distributed experimental data to validate such models has been lacking.

A range of studies have been carried out on PEFC electrodes and hardware concerning *in-situ* measurements of in-plane distributions of various quantities [49–54]. *In-situ* measurements within the PEFC's membrane-electrode assembly have been limited. Prior work includes using Pt-wire probes embedded in the membrane to measure the presence of hydrogen peroxide [55,56], oxygen and hydrogen concentrations [52,53,57], and water content [58]. Some of these studies featured multiple probes embedded through the thickness of the membrane to obtain through-plane measurements [53,55,58]. Perhaps the most relevant of these studies to this work are those that amperometrically sensed oxygen concentrations at the cathode CL/PEM interface [52,56,57], one of which did so with multiple probes across the plane of the PEM to obtain in-plane distributions [52]. Other researchers have applied oxygen sensitive paints on transparent plates to measure oxygen concentration along the gas channels and the DM surface [59]. Unfortunately, optical techniques are not amenable to microscale measurements within the porous components. To our knowledge, only one prior existing study reports distributed oxygen concentration measurements through the thickness of DM [60]. However, this intrusive approach first involved milling a large 100 μm hole through the entire DM and then inserting a 45 μm diameter fiber optic sensor through that hole. Thus, the effects of sub-100 μm features and, more critically, the restricted diffusion of the small pores in the MPL are not resolved.

In this paper, we present the *in-situ* characterization of oxygen transport through the diffusion medium (DM) of a working polymer electrolyte fuel cell (PEFC) using an oxygen concentration microsensor. The slender microsensor had a 25 μm tip diameter, made from a pulled glass capillary, which allowed us to measure concentrations within the DM pores. The 25 μm tip diameter is significantly smaller than the characteristic fiber spacing in the DM's carbon fiber felt and should not significantly affect the DM's microstructure or transport, yielding minimally intrusive measurements. Wargo et al.'s [47] pore size characterization showed in-plane chord length distribution peaks that were slightly larger than 50 μm in the fiber domain, which is twice the sensor diameter. The sensor tip diameter is also only twice that of the DM's carbon fibers, so its presence should not significantly impact oxygen transport relative to the existing materials, which include dense bundles of fibers. The sensor can also pass through the MPL, as first tested *ex-situ*, only affecting transport locally after the experiment is fully complete as we will discuss.

Using a precision stage with a micromanipulator, we measured the spatial distribution of O₂ concentration at 20 μm resolution through the thickness of unmodified commercial DMs in operating PEFCs. We performed these measurements at different current densities and different values of relative humidity (RH), on multiple fuel cell builds. We then analyzed those concentration measurements to yield position-dependent transport properties through the DM thickness, measured here *in-operando* for the first time, and to find where liquid water appears in the DM under different conditions, measured here *in-operando* for the first time using a non-imaging-based method. Finally, since the transport properties of a porous medium arise from its microstructure, we employed microscale X-ray computed tomography (micro-CT) to characterize the morphology of the DM and give further insight to the results of the oxygen concentration analysis.

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