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X-ray Tomographic Analysis of Porosity Distributions in Gas Diffusion Layers of Proton Exchange Membrane Fuel Cells

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ABSTRACT

This paper describes a method to characterize the structure of polytetrafluoroethylene (PTFE) treated gas diffusion layers (GDLs) with and without microporous layers (MPLs) using 3D X-ray micro computed tomographic (μCT) microscopy. In this work, the structure of single and dual layer GDLs is evaluated via μCT for various GDL samples (such as Toray TGP-H-060 and AvCarb EP40) loaded with different MPLs. A new method is presented for separating, or segmenting, the various phases of the GDL, i.e., void space, carbon fiber (including binder and PTFE), and MPL. Through analysis, it was found that the variation in bulk porosity and the average pore diameter of the GDLs depends highly on the GDL series manufacturing and treatment processes. Using advanced image analysis techniques, routines were developed to accurately segment the GDL fibers (including binder/PTFE) and the MPL. The percentage of the intruding MPL material into the carbon fiber paper as a function of the GDL thickness was successfully found for dual layer GDLs, with varying PTFE content and areal weight loading in the MPL. This analysis provides invaluable insight into the physical microstructure of paper-based GDLs, emphasizing the heterogeneous porosity distribution of single layer GDLs and the interaction of the MPL with the carbon fiber paper of dual layer GDLs.

1. Introduction

The proton exchange membrane fuel cell (PEMFC) has recently received significant attention from the automotive industry as a clean and efficient energy system with a significant potential for development and integration into transportation systems [1–3]. A PEMFC creates electrical power through the electrochemical reduction-oxidation reaction of a fuel and an oxidant. Commonly, hydrogen gas is used as a fuel at the anode and oxygen gas (or air) is used as an oxidant at the cathode, with only heat and water as by-products of the reaction. The anode and cathode electrodes each consist of a catalyst layer (CL), a gas diffusion layer (GDL), and a bipolar plate. The electrodes are separated by a perfluorosulfonic acid (PFSA) membrane that allows for proton exchange from the anode to the cathode, while electron transfer occurs through an external load. The PFSA membrane, layered with a CL and GDL on both sides, forms the membrane electrode assembly (MEA), which is the core of a PEMFC. Reactant gases are transported through a flow field in the bipolar plate to their respective electrodes of the MEA and are then diffused through the GDLs to the CLs, which is where the reduction-oxidation reaction occurs. The ineffective transport of reactants to, and removal of products from, the reaction sites on the CLs can lead to mass transport issues within the cell which, in turn, lead to decreased performance, especially in high power density regions [3,4].

The GDL of a PEMFC is an integral layer which enhances the diffusion of reactant gases from the flow field to the CL of the respective electrodes [4,5]. This porous carbon layer is important for the electrical connection and heat dissipation between the CL and bipolar plate; while it also acts as a mechanical support for the MEA [3]. Another key process occurring in the GDL is the mitigation of the water produced at the cathode by the electrochemical reaction [6]. In essence, the GDL must remove excess water to avoid flooding of the electrodes, while the PFSA membrane must be kept well hydrated to maintain high proton conductivity [3]. To ensure this proper water saturation balance, it is necessary to understand the structural properties and the two-phase flow of reactant gas and water within the GDL to help with mitigation strategies for improving mass transport properties [3,6].

The GDL is composed of carbon fiber strands (dia. ~7 μm) manufactured into a sheet-like product [7]. The fuel cell community commonly uses three different GDL types: paper-,

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felt-, and cloth-based. The main difference between these GDLs is the mechanisms in which the carbon fibers are held together in the manufacturing process, as described in detail by Mathias et al. [7]. Paper-based GDLs consist of carbon fibers, machine laid and bound together by a chemical binder. This is followed by impregnation of a carbonizable thermoset resin and a heat-treatment process for carbonization/graphitization of the resin and carbon fibers. The dried resin acts as a binder to hold the carbon fibers together and the heat-treatment process helps to improve electrical and wetting properties. Another approach for paper-based GDLs is to add a carbon or graphite powder to the resin binder in the paper making process to help further improve the electrical properties and also impart hydrophobic properties to the material [7].

To ensure that pores do not become flooded with liquid water, leading to impeded gas diffusion, GDLs are commonly treated with hydrophobic coatings such as polytetrafluroethylene (PTFE) and/or microporous layers (MPLs). The untreated (unteflonated) or treated (teflonated) macroporous carbon fiber paper substrate is referred to as a single-layer GDL, while a GDL with an MPL is referred to as a dual layer GDL [4]. The single layer GDLs are commonly impregnated with an aqueous PTFE dispersion to increase hydrophobicity, followed by a drying and heat-treatment process to remove the remaining solvent, fix the PTFE, and carbonize the constituents [7]. The MPL within the dual layer GDLs consists of a carbon black powder and a hydrophobic agent (commonly PTFE) applied to one or both sides of the carbon fiber substrate. After application of the MPL, the dual layer GDL is taken through additional drying and heat treatment processes [7]. The addition of an MPL serves to improve water management and electrical contact between the GDL and CL [2,4]. Together, the addition of MPL and PTFE has been repeatedly proven to significantly increase PEMFC performance, especially in regions of high current densities [4,5,8–10].

A number of recent studies have provided new insight into the physical structure of the GDL. The chief metrics for characterization are related to the pore size distribution (PSD) and bulk porosity, since these features directly affect the GDL's mass transport properties [11]. There are two main methods used to characterize these properties: mercury intrusion porosimetry (MIP) and capillary flow or method of standard porometry (MSP). MIP provides volumetric information about the PSD of the GDL, while MSP determines the PSD of only the smallest diameter of a tortuous path (throat of through-pore) within the GDL. As mentioned in Arvay et al. [3], MSP may serve as a better method for measuring PSD than MIP since it uses a much lower pressure and therefore has less chance of distorting pores or destroying the GDL sample [3,11]. A typical graph of the PSD measurement of a GDL reveals a bimodal distribution with micropores and macropores. The micropores can be explained by voids formed in the hydrophobic coatings (i.e., voids in the binder/PTFE or voids between carbon nanoparticles within the MPL); whereas the macropores represent the pores formed between the GDL carbon fiber strands or large cracks within the MPL [3,8,9].

Han et al. [8] combined Scanning-Electron Microscopy (SEM) and MIP to characterize the pore structure of single layer Toray TGPH-030 GDLs with 20 wt% PTFE content. The authors found a bimodal PSD with a smaller peak at 85 nm (representing micropores formed by small agglomerates within the binder and PTFE) and a larger and broader peak at 40.3 μm (representing macropores formed by the carbon paper) [8]. This study also looked at embedding the carbon paper with a mixture of carbon particles and PTFE, which was called a carbon-filled GDL (CFGDL). Their results showed that the total porosity of single layer and CFGDLs were 77% and 67%, while the average pore diameters were 35.8 and 4.7 μm. In-situ testing confirmed an increase in cell performance using the CFGDL as compared to the single layer GDL, especially around limiting current densities. The authors attributed this increase to the preferential formation of micro-water droplets within the modified microstructure of the CFGDL, which reduces mass transport losses [8]. This study demonstrates the importance of the optimization of the GDL parameters for maximum fuel cell performance.

Phillips et al. [12] characterized untreated and treated, single layer paper-based GDLs through the ex-situ measurement of transport properties such as wettability, pore size distribution (PSD), and permeability. Using MSP, it was found that the average pore diameters for the samples of Toray TGP-H-060 with PTFE levels of 0, 6, 19 wt% decreased only slightly from 33, 30.5, 29 μm, respectively. Based on these results [12] and those presented in [7,8–10,13], it has been found that the amount of PTFE applied affect several mass transport characteristics within PEMFCs, and can greatly enhance their performance.

Parikh et al. [11] used image analysis techniques to obtain a PSD from 2D SEM images for different single layer GDL types (Freudenberg H2315 non-woven, SGL 25 BC with 5% PTFE, and TGP-H-060 with 7% PTFE). They found a considerable variation in the pore sizes, shapes and clustering between different GDLs, with the average pore size ranging from 16.5 μm for the Freudenberg, 31.83 μm for the SGL, to 26.4 μm for Toray. These results are in good agreement with the results obtained from MIP and MSP techniques [8,9,11,12]. In an effort to understand the 3D structure of the GDL, a stochastic model has been used in [11] to construct a 3D realization of the studied GDLs based on the 2D SEM images and pre-determined pore parameters. The authors suggest that the 3D geometry should be used in modeling to yield a more representative behavior of the two-phase flow in the GDL. Additionally, they proposed that the GDLs microstructural properties should not solely be characterized by PSD, but also by pore shape and clustering of pores in the interconnected porous network of the GDL [11].

The above studies utilize bulk methods (i.e. MIP and/or MSP), along with 2D SEM imaging, to characterize the porosity and PSD of GDLs. However, it is inherently known that GDLs have a complex porous 3D structure that can vary in the in-plane (IP) and through-plane (TP) directions. High-resolution X-ray computed tomographic microscopy (μCT) techniques have been increasingly utilized in recent years as a valuable tool for visualizing and understanding the complex 3D microstructure of the GDL.

In a primary study, Sinha et al. [14] used μCT to image the liquid water distribution in a GDL, and thus to obtain a liquid saturation curve across the GDL thickness. Further, Buchi et al. [15,16] have used μCT to obtain the local water saturation level across the GDL thickness for different water pressures. Other similar studies have proven μCT to be useful in the imaging and analysis of the water configuration within the GDL [6,17,18]. Using μCT, Markotter et al. [19,20] have shown vivid visualizations of the water transport paths in the GDL with an in-situ PEMFC setup after ceasing the reactant flow. μCT has also been used to show the effects of the PTFE content in the GDL [21], to study the effect of compression on the GDL morphology [22,23], to identify and segment the MPL within the GDL [24], and to visualize the entire membrane electrode assembly (MEA) [25]. Kim et al. [26] have used μCT to study the porosity variation of paper-based and felt-based GDLs under freeze-thaw cycles and have also provided an extensive review on the evaluation of water management using μCT [27]. These studies show significant value as they can be used for numerical models and also for understanding the microstructural transport parameters of the GDL [22,28].

Bazylak and coworkers [6,29–33] have provided substantial insight into the structure of the GDL by using μCT to acquire a 3D image of the structure of the GDL and then to characterize the