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Gas-diffusion-layer structural properties under compression via X-ray tomography

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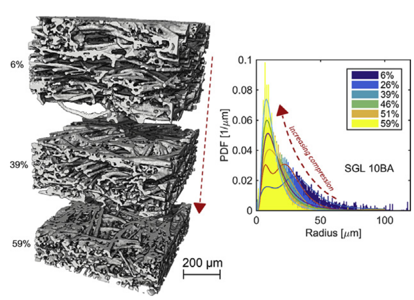
HIGHLIGHTS

- X-ray CT used to investigate morphological properties of GDLs.
- Porosity, tortuosity and PSDs reported under compression.
- GDLs heterogeneity was studied with ellipsoid factor.
- Representative elementary volume was defined for GDLs, which was 1 × 1 mm.

GRAPHICAL ABSTRACT



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ABSTRACT

There is a need to understand the structure properties of gas-diffusion layers (GDLs) in order to optimize their performance in various electrochemical devices. This information is important for mathematical modelers, experimentalists, and designers. In this article, a comprehensive study of a large set of commercially available GDLs' porosity, tortuosity, and pore-size distribution (PSD) under varying compression is presented in a single study using X-ray computed tomography (CT), which allows for a noninvasive measurement. Porosities and PSDs are directly obtained from reconstructed stacks of images, whereas tortuosity is computed with a finite-element simulation. Bimodal PSDs due to the presence of binder are observed for most of the GDLs, approaching unimodal distributions at high compressions. Sample to sample variability is conducted to show that morphological properties hold across various locations. Tortuosity values are the lowest for MRC and Freudenberg, highest for TGP, and in-between for SGL papers. The exponents for the MRC and Freudenberg tortuosity demonstrate a very small dependence on compression because the shapes of the pores are spherical indicating minimal heterogeneity. From the representative-elementary-volume studies it is shown that domains of 1 × 1 mm in-plane and full thickness in through-plane directions accurately represent GDL properties.

1. Introduction

Gas-diffusion layers (GDLs) find application in various electrochemical technologies including polymer-electrolyte fuel cells (PEFCs) and redox flow batteries (RFBs) [1–8]. For these devices to reach commercialization, cost reduction and performance

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optimization are required [1,3]. PEFCs with novel thin-film electrodes, such as 3M's nano-structured thin-film (NSTF) electrodes have reduced platinum (Pt) electrocatalyst loading and have demonstrated high power-densities; however, water-management during start-up and at lower temperatures is a significant challenge [1,9–13]. In PEFCs, water is formed in the cathode and is removed through porous GDLs that provide structural support for membrane electrode assembly, delivery of gas reactants, electron and heat transport, and removal of product water [14,15]. In RFBs, they also have the added functionality of providing a catalytic surface [5–7]. Understanding morphology and transport properties of these porous layers is essential for optimizing water management, mass transport, and performance in these devices.

GDLs are fabricated using polyacrylonitrile (PAN) polymer, which is carbonized by heating in a range of 1200–1350 °C in nitrogen [16]. For most of the GDLs, the polymer matrix is bound together chemically with carbonaceous binder (paper GDLs) or mechanically (woven GDLs). The resulting carbon fibers have diameters of 6–8 μm and wide pore-size distribution (PSD) with a mean radius in the range of tens of micrometers [16]. Commercial GDLs have a thickness in the range of 190–440 μm and are anisotropic because of fiber in-plane preferential orientation during roll-to-roll processing. In the last fabrication step, the GDL is made hydrophobic, typically by infiltration of polytetrafluoroethylene (PTFE) or perhaps by direct fluorination [4].

Various morphological metrics can be used to characterize the structure of GDLs and effective transport parameters. Porosity, PSD, and tortuosity are three major characteristics from which effective transport properties can be derived indirectly [17–20]. Porosity is defined as a ratio of void volume to total volume and it is relevant for gaseous and water transport. Knowledge of porosity is needed to model gas transport and liquid permeability accurately as effective diffusivity and permeability are directly proportional to it [18,21]. Many experimental techniques have been developed to measure GDL porosity, which is challenging due to their thin, compressible, and inhomogeneous geometry [22,23]. These techniques include gas pycnometry [22,23], mercury intrusion porosimetry (MIP) [24–26], weighing [17,27], and buoyancy [20]. A detailed comparison of these methods is given by Rashapov et al. [20], where shortcomings of the methods are mainly due to the inability to resolve the interfacial porosity properly, and limitations of these techniques for a single, thin GDL layer. Moreover, these techniques are limited for measuring the porosity of a free-standing GDL and cannot be applied for compressed GDLs, as they exist in assembled cells. For example, to estimate the porosity of a compressed GDL, empirical relationships are used that linearly interpolate or extrapolate compressed porosities assuming the solid fraction does not change [17,23].

PSDs are useful for obtaining water-retention curves [24,28], which are plots of capillary pressure vs. liquid-water saturation. For hydrophobic media, a non-wetting fluid will intrude voids with larger pore diameter and progressively fill the smaller voids at higher capillary pressures. Therefore, knowing GDL PSDs is essential in predicting water transport through these layers. MIP is the most common method of measuring PSDs of GDLs, where a sample is submerged in mercury (completely non wetting) and at each increasing capillary pressure mercury is forced into smaller pores [24–26]. Thus, capillary pressure and volume are recorded and the PSD obtained. One of the challenges of this method is the necking effect, where a large void behind a narrow neck is mistakenly attributed to a volume of a narrow pore. There is a need for an alternative method for PSD that is more reliable and non-invasive.

A GDL's tortuosity is generally extracted from measurements of effective gas diffusivity. A variety of experimental set-ups have been developed to study the diffusivity of the GDLs [17–19,29–34]. These include a Loschmidt cell, electrochemical impedance spectroscopy, and gradient methods (e.g., water vapor, limiting current density, or local chemical sensors). These techniques have been mostly applied to study conventional GDLs and primarily concentrated on through-plane effective diffusivity. Effective media theories and computational models exist as well to predict gas transport through GDLs [28,35–41]. Several recent efforts extended Bruggeman's theory, which is applicable for homogeneous porous media with spherical voids or solids, to represent a GDL's inhomogeneity by allowing for a number of particle shapes and orientational anisotropy [40,42]. Many of the computational efforts concentrate on generating a GDLs structure stochastically by using bulk properties such as porosity, fiber diameter, and percentage of binder as fitting parameters [36,41,43]. Numerical models are then applied to these generated structures to extract effective transport properties. Alternatively, a selected class of models utilized direct reconstructions of the GDL domains from available three-dimensional X-ray CT images [37,38,44].

X-ray CT allows one to resolve the internal structure and inhomogeneity under controlled conditions including compression [14,39,45–53]. This technique is straight-forward and virtually error-free as the only source of error is due to a threshold selection that separates pore from fiber and binder. To the best of authors' knowledge, X-ray CT is the only feasible technique to resolve porosity and pore structures under compression and at various regions within the GDL (either in plane or through thickness). This technique has been used to measure GDL properties in limited studies including spatially-resolved porosity [50,52,54,55], effects of compression [14,53,54] and water distribution [37,14,49,52]. Many of these studies focused on a single GDL or property, and a comprehensive comparative study with various information is missing. Moreover, differential PSDs for GDLs under various compressions have not been reported previously.

In this paper, we use X-ray CT and computational models to characterize the morphology of various commercial GDLs under different levels of compression and PTFE loading to uncover underlying relationships and trends and provide data for modeling and GDL designers including spatial porosity, PSD, and ellipsoid factor. In addition, we also explore the issue of representative elementary volumes (REVs) for GDLs, which is the smallest volume of the sample that retains the bulk properties [56], a critical parameter in terms of analysis and utilization that cuts across various experiments and theory.

2. Methods and materials

2.1. Experimental setup

The tomography experiments for the GDL characterization were conducted at Beamline 8.3.2 at the Advanced Light Source (ALS). A double-multilayer monochromator was used to select 14 keV X-rays, and detection was with a 0.5 mm LuAG scintillator and 5× lenses with a sCMOS PCO. Edge camera, giving a 1.33 μm pixel dimension, and a 3.3 mm horizontal field of view (FOV). Using a 300 ms exposure time yielded 8000 counts on the 16-bit camera (allowing a maximum of 65535 counts). For each tomographic scan, 1025 projections were acquired over a 180° rotation, with a total scan time of 7 min.

The schematic of the sample holder is shown by Fig. 1. The sample-holder consists of an aluminum stage, and a high X-ray transmitting Vespel® cup with wall thickness less than 1 mm. A 3.2 mm diameter circular GDL sample was cut and pressed against the aluminum stage with a flat stamp. After the sample was mounted on the stage, an ultra-fine pitch thread was used to control GDL compression.