Journal of Power Sources 355 (2017) 8–17

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Multi-scale structural analysis of gas diffusion layers

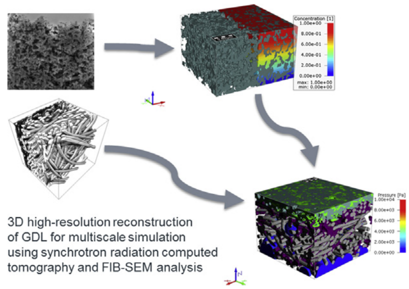
Martin Göbel [a, *], Michael Godehardt [b], Katja Schladitz [b]

[a] *Volkswagen Aktiengesellschaft, 38436 Wolfsburg, Germany*
[b] *Fraunhofer Institute for Industrial Mathematics, ITWM, Fraunhofer-Platz 1, 67663 Kaiserslautern, Germany*

HIGHLIGHTS

- Synchrotron X-ray tomography and FIB/SEM analysis of GDL microstructure.
- 3D imaging and image-processing of GDL microstructure.
- Multi-scale micro simulation of GDLs.
- Prediction of macroscopic material properties from GDL microstructure.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 October 2016
Received in revised form
19 March 2017
Accepted 20 March 2017

Keywords:
Gas diffusion layer
Micro porous layer
Computed tomography
Synchrotron radiation
Multi-scale simulation
Micro-tomography
Nano-tomography
Image segmentation
3D image processing

ABSTRACT

The macroscopic properties of materials are strongly determined by their micro structure. Here, transport properties of gas diffusion layers (GDL) for fuel cells are considered. In order to simulate flow and thermal properties, detailed micro structural information is essential. 3D images obtained by high-resolution computed tomography using synchrotron radiation and scanning electron microscopy (SEM) combined with focused ion beam (FIB) serial slicing were used. A recent method for reconstruction of porous structures from FIB-SEM images and sophisticated morphological image transformations were applied to segment the solid structural components. The essential algorithmic steps for segmenting the different components in the tomographic data-sets are described and discussed. In this paper, two types of GDL, based on a non-woven substrate layer and a paper substrate layer were considered, respectively. More than three components are separated within the synchrotron radiation computed tomography data. That is, fiber system, polytetrafluoroethylene (PTFE) binder/impregnation, micro porous layer (MPL), inclusions within the latter, and pore space are segmented. The usage of the thus derived 3D structure data in different simulation applications can be demonstrated. Simulations of macroscopic properties such as thermal conductivity, depending on the flooding state of the GDL are possible.

1. Introduction

One of the most promising alternative propulsions in automotive industry are fuel cells based on proton-exchange-membranes (PEMFC). Key issues for the acceptance of PEMFC are improvements of power density, durability as well as cost reduction. Liquid water accumulation and transport are key aspects in operating PEMFC's efficiently. To optimize the design for performance and durability, the water management of the gas diffusion layer (GDL) has to be understood. GDLs affect the water distribution

* Corresponding author.
E-mail address: martin3.goebel@audi.de (M. Göbel).

http://dx.doi.org/10.1016/j.jpowsour.2017.03.086

throughout the fuel cell and must be characterized in terms of material properties and geometry. While a humidified environment is beneficial for ionic conductivity of the membrane, the saturation of pores in the GDL with liquid water blocks the transport of the reactants to the catalyst. Condensation of the produced water during the electrochemical reactions can be expected to occur especially under high current density operation. Efficient operation requires several functions of the GDL: pathways for reactants and byproduct water, thermal (properly designed) and electrical conductivity (as high as possible), mechanical support to the membrane and flow field. To meet those requirements, not only knowledge about macroscopic properties as stiffness, compressibility and conductivity is vital, but also a fundamental understanding of the micro structure geometry and composition of the porous GDLs [1–4].

GDLs commonly used in PEMFCs comprise graphitized carbon fibers and carbonized resin. They are usually treated with polytetrafluoroethylene (PTFE) to increase hydrophobicity. For fuel cells used in automotive industry, two basic structure types of GDLs are used; paper- and felt-based (non-woven). The main difference between these GDL types is the mechanism, how the carbon fibers are held together in the GDL structure. Paper-based GDLs consist of carbon fibers interconnected by a binder. During a heat-treatment, the binder resin is repeatedly carbonized and graphitized. The carbon fibers on felt-based GDLs are matted together for mechanical consolidation usually through a hydro-entangling process. It is common to add a micro porous layer (MPL) onto the GDL substrate to enhance fuel cell performance especially for high current densities. The MPL typically consists of carbon and/or graphite particle agglomerates mixed with a polymeric binder, which is applied to the interface between the GDL and the catalyst coated membrane (CCM). MPLs feature pore sizes in the size range of the carbon agglomerates, between 100 and 500 nm, as compared with 10–50 μm pore size for the GDL substrates. The distribution of carbon fibers as well as their 3D geometry within a GDL has been challenging to observe directly by visible light microscopy. In order to resolve the complex structure, state-of-the-art 3D imaging techniques were applied.

Advanced, X-ray based computed tomography methods have recently been employed on GDLs to reveal the 3D micro structure achieving a wide range of spatial resolutions and contrast between GDL material and void. For a standard μCT scan, the sample is placed on a rotation stage and illuminated while rotating. The transmitted radiation is recorded by a flat panel detector. The resulting projection images represent essentially the attenuation of the sample. From the projection images taken at different angles of view, the internal mass distribution of the sample is reconstructed cross-sectional slice by cross-sectional slice, yielding a complete tomographic volume image. The intense flux of synchrotron light sources allows to increase contrast using phase-sensitive imaging, measuring rather local electron density than local mass density like in absorption-based X-ray imaging. For a more detailed overview and a more thorough discussion of the respective advantages of using laboratory μCT devices or a dedicated imaging beamline at a synchrotron facility, see Ref. [5]. The improvement of instrumentation in the recent years allowed imaging of GDLs at resolutions well below 1 μm by synchrotron-radiation-based tomography (SRμCT) [6–10].

In order to spatially image the nano-scale porous carbon black structure of MPLs, too, dual-beam FIB-SEM [11–15] or nano computed tomography [16] can be applied. FIB-SEM is a serial slicing method. More precisely, a focused ion beam (FIB) is integrated into a scanning electron microscope (SEM). Alternating slicing and SEM imaging, this device yields 3D images at SEM resolution.

To predict macroscopic material properties, such as thermal conductivity or effective diffusivity, micro structure simulation approaches have been developed [17]. Experimental high resolution 3D structure data are essential input for those simulations. Structural information from the two scales has been combined to feed multi-scale simulations of macroscopic properties [18–20] while the FIB-SEM image data serve only as a validation tool in Ref. [21].

In this paper high-resolution hard X-ray CT and combined FIB-SEM measurements on two GDL types were performed. Based on the SRμCT images, substrate, binder/impregnation, MPL, and inclusions within the MPL, as well as the pore space are segmented for one of the two considered GDL types. This is more detailed than other recent work, like [21], where active material and binder are separated using a combination of adaptive gray value histogram equalization, double thresholding, and morphological post-processing, or [10] combining gray value thresholding with morphological transforms to segment into substrate, MPL, and pore space. The FIB-SEM images are segmented into MPL (carbon black and PTFE) and pore space using an adaption of the algorithm from Ref. [14]. Further segmentation of the MPL into carbon black, PTFE, and pore space has been achieved in Ref. [16] exploiting slight gray value differentiations in nano-CT images and pre-knowledge of the respective volume fractions.

The usage of 3D structure data in different simulation applications is demonstrated. Due to the achieved more detailed structural characterization, it is possible to model flow through GDL using direct simulation [22,23].

2. Experimental

2.1. Materials

In this study, FREUDENBERG® H14C7 (referred to as H14C7 in the following) and SGL SIGRACET® 28BC (referred to as 28BC in the following) were selected to analyze the regions of interest. Fig. 1 shows microscopic images of the samples used at 500× magnification at substrate side and 1000× at MPL side. H14C7 is a non-woven, felt-based GDL with MPL and has an uncompressed thickness of 175 μm. The substrate is treated with 10 % wt PTFE for higher hydrophobicity. The areal weight is 100 g/m^2. The used MPL is a mixture of carbon components, PTFE dispersion, surfactant and solvent. 28BC is a paper based GDL with a 5 % wt PTFE treatment and an additional MPL. The uncompressed thickness and areal weight are 235 μm and 100 g/m^2, respectively. The cracks in the 28BC MPL are characteristic.

2.2. Synchrotron radiation micro-computed tomography

Synchrotron-based micro-tomography in combination with hard X-ray phase contrast was applied in order to exploit the higher sensitivity and better signal-to-noise ratio that this imaging technique offers compared to μCT with laboratory devices [24].

For samples consisting of materials with low atomic numbers (low-Z materials) absorption-based techniques yield only a weak contrast and thus do not depict fine details or differentiate components. Therefore, X-ray phase contrast was used, enabled by the partial spatial coherence of the X-ray beam available at synchrotron light sources. Interfaces (edges) within the sample are emphasized as they refract the x-ray-wave when a drift space is left between sample and detector (propagation-based phase contrast) [25–27]. Depicting the local refraction of a specimen instead of the local density-related attenuation drastically increases sensitivity: the real part of the refractive index is orders of