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Micro-porous layer stochastic reconstruction and transport parameter determination

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HIGHLIGHTS

- A novel stochastic model was developed to generate realistic 3D MPL structures.
- The model was successfully validated against experimental data.
- We calculated effective transport properties that are challenging to measure.
- Relationships between MPL morphology and properties were determined.
- We propose a new design tool to guide the development of improved MPL materials.

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ABSTRACT

The Micro-Porous Layer (MPL) is a porous, thin layer commonly used in fuel cells at the interfaces between the catalyst layers and gas diffusion media. It is generally made from spherical carbon nanoparticles and PTFE acting as hydrophobic agent. The scale and brittle nature of the MPL structure makes it challenging to study experimentally. In the present work, a 3D stochastic model is developed to virtually reconstruct the MPL structure. The carbon nanoparticle and PTFE phases are fully distinguished by the algorithm. The model is shown to capture the actual structural morphology of the MPL and is validated by comparing the results to available experimental data. The model shows a good capability in generating a realistic MPL successfully using a set of parameters introduced to capture specific morphological features of the MPL. A numerical model that resolves diffusive transport at the pore scale is used to compute the effective transport properties of the reconstructed MPLs. A parametric study is conducted to illustrate the capability of the model as an MPL design tool that can be used to guide and optimize the functionality of the material.

1. Introduction

The Micro-Porous Layer (MPL) is a commonly used component in the fabrication of Proton Exchange Membrane Fuel Cells (PEMFCs). It is a porous thin layer generally composed of carbon nanoparticles and hydrophobic agent, most commonly PTFE [1–3]. It is used as an intermediate layer between the Gas Diffusion Layer (GDL) substrate and the catalyst layer. The MPL is made by mixing an ink of carbon particles, PTFE, a solvent, and in some cases a pore forming agent [1–4]. The solution is then applied to the GDL substrate with different techniques, most commonly spraying and screen printing, followed by drying and sintering [2].

Several studies have been conducted to determine the role of the MPL in PEMFCs and its impact on the performance [1,2,5–12]. The MPL allows a smooth transition between the rough, macroporous structure of the GDL substrate and the more uniform, microporous catalyst layer [1,12]. The presence of the hydrophobic agent in the MPL allows the catalyst layer and membrane to retain adequate hydration especially for low current density operation. In most of the cases the presence of the MPL impacts positively the water management within the fuel cell [9,12,13]. Other studies have shown that MPL cracks can provide routes for evacuation of liquid water to avoid catalyst layer flooding at high current densities [14–16]. In the latter case, the transport of gas reactant and water vapor will be mainly facilitated via the bulk material of the MPL,

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thus the bulk properties of the MPL are essential to understand its impact on the fuel cell performance.

Studying the transport properties in the bulk of the MPL structure is a considerable challenge. The porous layer is very brittle and mechanically unstable which limits the possibilities for measuring its properties experimentally. Some experimental studies have been conducted on both the MPL and GDL substrate assembled together [4,17–24]. The properties of the MPL were then deduced by subtracting the properties of the GDL substrate measured separately [17,18,20,23]. Other characteristics such as the Pore Size Distribution (PSD) have been measured by coating the MPL on a non-porous substrate material [25].

Recently, the MPL was characterized using focused ion beam scanning electron microscopy (FIB-SEM) to obtain a series of 2D images and reconstruct the 3D structure [25–27]. Subsequently, computational methods were applied to the resulting structure to calculate the effective transport properties. This approach provides an accurate representation of the structure of a physical MPL sample and allows estimating its main effective transport properties. However, this method is presently unable to distinguish between the carbon and PTFE phases, although it provides reliable results for the transport properties within the pores.

Two previously published works demonstrated stochastic modeling of the carbon particles of the MPL without considering the PTFE phase [28,29]. Becker et al. [28] generated an MPL based on agglomerates of 200 spherical carbon particles that were slightly overlapping. The 3D virtual MPL structure was used to obtain bulk properties in the framework of a multi-scale approach to compute the properties of the GDL and the MPL together. Zamel et al. [29] used a similar approach to study the thermal conductivity of the MPL. The structure was reconstructed by generating the pores first (represented by large overlapping spheres) and adding the carbon particles in the remaining space outside of the pore phase. At the last step of the simulation, the small space between the spherical carbon particles was turned into solid and glued the structure together.

The objective of the present work is to develop a stochastic model specifically tailored for MPLs that can be used as a comprehensive design tool for material development assignments in order to enhance the functionality and manufacturability of the MPL. Numerical simulations are ideal for this purpose to accelerate and reduce the cost of the design process. The proposed stochastic model is designed to capture the real morphology of the MPL material, and to distinguish carbon nanoparticles, PTFE, and pore phases. With these features, the model is coupled to a pore scale transport model to enable in-depth analysis of effective transport properties and their correlations with practical fabrication parameters. In the next section, a description of the model is provided and the key parameters are explained. Then, the validation process and simulated results are presented and discussed. The results of a parametric study are also presented and analyzed.

2. Model description

The MPL porous structure considered in this work is made of spherical carbon particles and PTFE. There are many different possible scenarios for the arrangement of particles while preserving a given porosity. However, the tortuosity and the average pore size will in general vary from one scenario to another, which will lead to different effective transport properties of the material. Through the model described in this section, the actual morphology of the MPL will be captured and validated using the PSD. Several parameters are introduced in the model to allow a certain level of control over the particle arrangement and to validate the structure with experimental data.

The selected domain size is 2 μm × 2 μm × 2 μm and initially filled with void space. The process of generating the MPL structure is conducted in two main steps: generation of carbon particles; and generation of PTFE. The reference material considered in this work has a porosity of 62% and a PTFE loading of 40% wt [25]. Using these inputs in addition to the densities of the materials, we can determine the volume of each solid phase. For example, for a total porosity of 62%, carbon particles will be generated until the porosity reaches 70%, and PTFE will then be added to reach 62% porosity.

All carbon particles are assumed to be spherical and have the same diameter. The stochastic process of generating the carbon phase is composed of two steps (Fig. 1):

1) Firstly, a small number of seed particles are generated and positioned randomly in the selected domain. These particles are not in contact with each other and are intended to be used as nucleation sites for the solid phase.
2) Secondly, the remaining carbon particles are added to the domain while ensuring physical contact with at least one pre-existing particle until the required amount of carbon particles is reached. The seed particles generated in the previous step are used as a starting point to grow the carbon clusters.

Three morphological parameters are introduced and controlled to obtain a realistic arrangement of the carbon particles:

- The fraction of particles used for seeding, α;
- The degree of overlap between particles in contact, δ; and
- The connectivity between particles, ζ.

These parameters were strategically chosen from the observations made from SEM images of the actual MPL and from the available knowledge of the fabrication process. They are meant to provide a suitable level of control over the morphology of the MPL structure while offering sufficient flexibility to simulate changes in the fabrication process. The first parameter α represents the size and distribution of the particle clusters. Increasing the number of particles used for seeding will increase the number of clusters and reduce their average size, which will influence the characteristics of the pore space (e.g., the PSD). The second parameter δ is used to represent the fact that the actual carbon particles are not perfectly spherical. The third parameter, the connectivity ζ, represents the average number of inter-particle contact points for each particle in the matrix. A high connectivity leads to more spherical and compact cluster shapes, while a low value (e.g., 2) leads to long, narrow chains of carbon particles. While these three parameters are varied, three other input parameters are considered to be fixed for each MPL material: the porosity, ε; the diameter of the carbon particles, d_p; and the composition defined by the weight fraction of PTFE, ω. These input parameters represent the constraints that will assure the generation of a unique structure for every set of the three morphological parameters α, δ, and ζ.

The PTFE is added as a binder to the carbon particles of the MPL to provide structural integrity and to increase the hydrophobicity of the layer. The MPL considered in this work is manufactured by mixing carbon particles, PTFE particles and a solvent. After coating, the mixture is subjected to a sintering process at 350 °C for 30 min to distribute the PTFE uniformly inside the porous structure [30,31]. Current characterization techniques do not allow discrimination between the carbon and PTFE phases [25], but with the sintering temperature being slightly above the melting point of the PTFE, the PTFE is expected to be preferentially located in the small pores between the carbon particles. Thus the PTFE phase is introduced into the carbon matrix structure within the narrow pore spaces