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An extended stochastic reconstruction method for catalyst layers in proton exchange membrane fuel cells

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HIGHLIGHTS

- A new stochastic reconstruction method for low Pt loading catalyst layers is developed.
- Controlling key structural parameters for agglomerates, ionomer, and Pt is allowed.
- Inhomogeneous catalyst layers with graded structural properties can be generated.

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ABSTRACT

This paper presents an extended, stochastic reconstruction method for catalyst layers (CLs) of Proton Exchange Membrane Fuel Cells (PEMFCs). The focus is placed on the reconstruction of customized, low platinum (Pt) loading CLs where the microstructure of CLs can substantially influence the performance. The sphere-based simulated annealing (SSA) method is extended to generate the CL microstructures with specified and controllable structural properties for agglomerates, ionomer, and Pt catalysts. In the present method, the agglomerate structures are controlled by employing a trial two-point correlation function used in the simulated annealing process. An off-set method is proposed to generate more realistic ionomer structures. The variations of ionomer structures at different humidity conditions are considered to mimic the swelling effects. A method to control Pt loading, distribution, and utilization is presented. The extension of the method to consider heterogeneity in structural properties, which can be found in manufactured CL samples, is presented. Various reconstructed CLs are generated to demonstrate the capability of the proposed method. Proton transport properties of the reconstructed CLs are calculated and validated with experimental data.

1. Introduction

Cost reduction, beside achieving sufficient durability, is a primary challenge for the massive commercialization of proton exchange membrane fuel cells (PEMFC) [1–3]. The cost can be reduced by lowering the applied dose of noble catalysts, mostly Pt, among other approaches. For the low Pt loading catalyst layers (CLs), the Pt utilization and the oxygen transport loss issues are critical to achieve a target performance. In order to develop the optimized CL that best utilizes the small amount of catalyst particles, a fundamental understanding of the influence of microstructures to the performance of cathode CLs has to be advanced. Due to current challenges in the experimental characterization of the microstructures and physical processes occurring in CLs [4–6], especially under working conditions, a high-fidelity computational study renders substantial advantages. The focus of this paper is on the reconstruction of 3-D CL microstructures for such computational studies.

Pore-scale simulations describe details of physico-chemical processes in reconstructed CLs and are suitable for advancing the fundamental understanding of microstructure-performance relations and thus for improving the CL performance through structure optimization. After a pioneering work of Mukherjee and Wang [6], various reconstruction methods have been developed for pore-scale simulations [5–11]. Initial works, including Mukherjee and Wang [6], used voxels as a unit element for a stochastic reconstruction process. The CL is typically assumed to consist of a mixed electrolyte/electron solid phase and pore phase. The random

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number generation method, the Gaussian random field (GRF) method, or the simulated annealing (SA) method is used to stochastically reconstruct a microstructure which has a specified structural property, for instance, a two-point correlation function [6,12–14]. The use of sphere particles as the unit element was proposed independently by Hattori et al. [15] and by Kim and Pitsch [9]. In Hattori et al. [15], carbon spheres are randomly placed, with the overlap being allowed, to form sphere clusters. Kim and Pitsch [9] proposed a Sphere-based SA (SSA) method, where spherical carbon particles randomly move in a stochastic optimization process, finding a structure with specified structural properties. In both works, the spherical carbon particles are assumed to be covered with uniform ionomer films. Recent developments in experimental imaging methods have advanced the characterization of the CL microstructures, providing structural information necessary for the reconstruction [5]. For instance, the nano-scale 3-D X-ray computed tomography (CT), which has a resolution of 30–50 nm [16,17], can be used to characterize the global agglomerate structure, but is not able to resolve pores within the agglomerates. A higher resolution can be achieved by the destructive 3-D scanning/transmission electron microscopic techniques (S/TEM). Currently, nano-scale focused ion beam (FIB) SEM has a maximum resolution of 10 nm along the thickness direction and 1 nm in the imaging planes [4,5,18,19]. However, the images are usually solid-pore two phases, and distinguishing the ionomer layer from the carbon structures [20] is still a challenging problem. The process-based reconstruction has also been proposed. For instance, Malek et al. [21] applied coarse grained molecular dynamics to simulate the spontaneous microstructure formation of each phase of a CL. Siddique and Liu [22] proposed a structure formation rule accounting for the physical fact that materials are likely to bound with each other to reduce surface energy. Their CLs grow from initial seed until the desired amount of deposited material of each phase is achieved.

In this paper, we present the extension of the SSA method for the optimization study of PEMFC CLs. In the optimization study, where the effects of structural parameters on the physico-chemical processes and the performance of CLs are investigated, of critical importance is the ability to control the microstructure of CLs during the reconstruction process. The SSA method can generate the CL microstructure for specified structural properties using the stochastic optimization approach and is therefore well suited for this purpose. However, like all other reconstruction methods as of now, the method needs to be extended for the reconstruction of customized, low Pt loading CLs, for instance, those mimicking experimental works [1]. Here, the SSA method is extended to generate the CL microstructures with specified and controllable structural properties for agglomerates, ionomer, and Pt catalysts. The agglomerate structures are controlled by employing a trial two-point correlation function used in the simulated annealing process. An off-set method is proposed to generate more realistic ionomer structures. The variations of ionomer structures at different humidity conditions are considered to mimic the swelling effects. A method to control Pt loading, distribution, and utilization is presented. The extension of the method to consider heterogeneity in structural properties, which can be found in manufactured CL samples, is presented. The proton transport properties of the reconstructed CLs at different humidity condition are calculated and validated with experimental data.

2. Stochastic reconstruction of catalyst layer

The catalyst layer of a PEMFC is usually composed of four phases: carbon agglomerates, electrolyte, catalyst particles, and pores. The carbon agglomerates provide electron pathways and support catalyst particles, typically platinum (Pt) or Pt alloy. They also contain primary pores through which gases and liquid water can flow. The electrolyte, typically Nafion ionomer, binds carbon agglomerates, and provides pathways for proton conduction and oxygen diffusion toward the catalyst surface. The secondary pores are the space formed between the agglomerates and provide primary pathways for oxygen and water in gas or liquid phase. The morphology of the CL influences the transport of the reactants and the products, which in turn has strong impact on the activity of the catalyst sites and overall CL performance, particularly at high current density in low Pt loading CLs.

In this work, we intend to develop a reconstruction method to use in the optimization study of low Pt loading CL. The method is developed through combining the SSA method for carbon structures with simple methods for generating realistic ionomer structures and catalyst particle distributions. The SSA stochastic optimization approach is used to find carbon agglomerate structures that satisfy specified structural statistical functions, thereby enabling the study of the effects of agglomerate morphology on the CL performance. The method is also extended to generate spatially heterogeneous and graded structures in a computationally efficient way. The ionomer structure is generated by taking into account various specified structure characteristics, including carbon coverage, thickness distribution, and volume fraction of ionomer at given relative humidity (RH) condition. An off-set method is proposed to generate a more realistic ionomer structure than the uniform impregnation approach. The catalyst particles are stochastically distributed after specifying the Pt loading, particle size distribution, and distribution characteristics over carbon particles. Detailed description of the reconstruction method is given as follows.

2.1. Carbon support

The carbon support structure is reconstructed by using the SSA method [9]. SSA is a stochastic method to reconstruct porous media with spheres as the elements in an optimization process. In the optimization process, spherical carbon particles randomly move to find a structure with specified structural properties. The overall procedure of the SSA method is briefly described below, while a detailed description can be found in Kim and Pitsch [9].

The reconstruction process is initiated by adding spherical carbon particles into the computational domain until the overall carbon volume fraction reaches a specified value, ε_s. The radius of the spheres is chosen based on the size distribution function, with the average radius of r_{cb}. The carbon volume fraction and the mean radius and size distribution of carbon spheres are usually given by experimental or manufacturing data [23,24], and can be varied as a part of the optimization process for CL microstructures. During the sphere addition step, the locations of the spheres are randomly selected while the overlap of spheres is allowed with a specified probability distribution function.

After the initialization, the optimization process starts by repetitively moving and relocating the spheres in the computational domain. The carbon structure continuously changes until its structural properties agree with the specified ones. In each iteration step, one sphere is randomly selected and relocated to a new position. The relocation is arbitrary and can be conducted in many ways, only affecting the convergence rate. For fast convergence, a specific probability distribution function for the relocation can be used. After each random movement, the energy or error function that measures the difference between the current status and the reference one is calculated: