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Stochastic reconstruction and a scaling method to determine effective transport coefficients of a proton exchange membrane fuel cell catalyst layer

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ABSTRACT

This work uses a method for the stochastic reconstruction of catalyst layers (CLs) proposing a scaling method to determine effective transport properties in proton exchange membrane fuel cell (PEMFC). The algorithm that generates the numerical grid makes use of available information before and after manufacturing the CL. The structures so generated are characterized statistically by two-point correlation functions and by the resultant pore size distribution. As an example of this method, the continuity equation for charge transport is solved directly on the three-dimensional grid of finite control volumes (FCVs), to determine effective electrical and proton conductivities of different structures. The stochastic reconstruction and the electrical and proton conductivity of a 45 μm side size cubic sample of a CL, represented by more than 3.3×10^{12} FVCs were realized in a much shorter time compared with non-scaling methods.

Variables studied in an example of CL structure were: (i) volume fraction of dispersed electrolyte, (ii) total CL porosity and (iii) pore size distribution. Results for the conduction efficiency for this example are also presented.

1. Introduction

In the near future the world's energy demand will have to be supplied using energy sources different from fossil fuels. Within such scenario hydrogen fuel could be playing an important role as an energy vector [1]. On the other hand, due to its high efficiency and the potential of being used in a great variety of applications, proton exchange membrane fuel cell (PEMFC) is being a much studied and developed technology in the last two decades [2,3].

Within a PEMFC, a catalyst layer (CL) is a small and thin region where electrochemical reactions take place as well as many transport processes, which to a large extent determine its general performance [4,5]. The solid phase of this component is formed by an electronic conductor which also serves as a support for a nanostructured catalyst, which should be in contact with a dispersed ionic conductor (ionomer) to complete the reactions [6]. This CL needs to be porous to allow the access of reactant gases entering the cell, and to let water formed by reactions exit the cell either in a vapor or in a liquid phase [7,8]. The porous medium also provides a large active area available for larger reaction sites and the resultant larger current [8].

In a PEMFC the catalyst is typically platinum (Pt), the supporting material most commonly used is carbon (C), while the ionomer is a polymer named nafion®. These materials will be referred to as CL's primary components. In a PEMFC CL the reactant gases are transported from the border between CL and the so-called gas diffusion layer (GDL) up to the reacting catalytic sites through pores formed during fabrication between the primary components. While the catalyst has the role of promoting the proper electrochemical reactions, the carbon collects and conducts the produced electrons and the ionomer should conduct protons generated or consumed by the proper reaction.

Experimental observations at the micrometer scale suggest that the CL is formed by agglomerates in a porous matrix [6]. The concept of agglomerates has been developed some years ago for electrochemical systems and it has been extensively applied to PEMFC [9–12]. Nevertheless, obtaining information at the nanoscale is very difficult using present experimental characterization techniques, which do not allow for the capture of images at that scale without modifying the original structure [13,14]. This limitation has lead to the formulation of different theories. The most popular is the theory that considers agglomerates as small spheres covered with a thin layer of ionomer and an inside of Pt/C particles [15–18].

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The structure and composition of a PEMFC CL define this component as a random heterogeneous material. This heterogeneity arises from the fact that it is constituted by different phases, being "phase" an identifiable domain with its own particular properties that differentiate it from the rest of the other phases in the CL (i.e. voids, other solid material, gases or liquids).

Proportionality coefficients for mass, energy and charge transport in a heterogeneous material are significantly affected by the properties of the phases from which this is composed, by the volume fraction composition, and by the structure of such phases. For this reason, an effective transport coefficient (ETC) is defined for a heterogeneous material as a proportionality coefficient, which characterizes the domain of the material. For a randomly formed heterogeneous material with M phases, a general ETC, K_e is:

$$K_e = f(K_1, K_2, \ldots, K_M; \phi_1, \phi_2, \ldots, \phi_M; \Omega) \quad (1)$$

where subscript of variables indicates a respective phase, K is the proportionality constant for that phase, ϕ is the phase volume fraction and Ω is a microstructural information of the domain [19].

In literature there are different mathematical relationships to determine ETCs [20–22]. For example, Maxwell-Garnett [21] developed a relationship to determine optical properties for diluted dispersions of uniform spheres. Later, Bruggeman extends Maxwell's model to systems with random dispersions of spherical particles with an extended range size [22].

A more recent and powerful technique to determine effective properties of random heterogeneous materials, is the so-called "stochastic reconstruction", which first applications is attributed to Quiblier [23]. This technique is based on the computational generation of a mesh that characterizes the real microstructure of the heterogeneous material, mathematically described by statistical functions referred to as "correlation functions". Torquato [19] offers a methodology to characterize microstructures, as well as fundamental theory to estimate effective properties. More recent works offer modifications to Torquato's methodology to optimize the quality in the stochastic reconstruction or to reduce convergence time during computing [24–27].

The right value of ETC is indispensable for an adequate numerical simulation of systems containing one or more components with characteristics of a heterogeneous media. An incorrect ETC value will alter the results and consequently it will provide a wrong interpretation of the transport phenomena.

On the other hand, PEMFC phenomena simulations have been of great interest in recent years due to the obvious advantages over experimental techniques: (1) lower research costs, (2) it is a powerful tool for the design of more efficient devices, and (3) it offers the possibility to better understand phenomena within the fuel cell in often unreachable places.

When the simulation objective is the prediction of gas flow field performance, it is common to assume the CL as a one-phase element [28–30]. Nevertheless, to detail the functioning of a CL, a mathematical approach has been used based on the assumption that a CL is a heterogeneous medium formed by agglomerates [11,31–33]. In this case, Bruggeman's approach is the most popular. The stochastic reconstruction has been successfully used in the simulation of a PEMFC CL. Wang et al. [34] proposed a direct numerical simulation (DNS) as a way to predict the CL's transport phenomena that take place at the micrometer scale. Unfortunately, the large number of control volumes required to detail the main elements that form the CL, in a computing domain that covers the whole electrode, makes DNS an expensive computation-wise method. Recently, Kim and Pitsch [17] proposed a "sphere-based simulated annealing" method, as well as the "lattice Boltzmann" method to reconstruct the microstructure of the CL in a PEMFC and to determine the effective diffusivity of the structure, respectively.

In this work a theoretical study of a PEMFC CL by the stochastic reconstruction of its microstructure and a scaling technique is presented. The scaling technique allows a significant reduction in computational resources needed for simulation. Scales are defined based on different observable structures at different order of magnitude scales. The reconstruction technique employed allows the use of information available before and after the manufacture of CLs. The so reconstructed structures are characterized with a two-point correlation function and its pore size distribution. Results obtained for the effective conductivity of theoretical samples with different nafion® content as well as different total porosity and pore size distribution are also presented. This work includes the following steps: (1) microstructure reconstruction at the different scale domains; (2) scaling strategy; (3) statistical characterization of the generated structures; and (4) analysis of ETCs by solving the charge transport equation. This technique can also be applied to evaluate the different structural theories.

2. Theory and calculation

In this section we describe the microstructural information and the perceptible scales of the CL. The mathematical analysis that conditions the grid generation (the statistical characterization and the ETC's determination) of a subdivided domain by n samples of inferior length scales is also presented.

2.1. Structural information and specific scales of CL in PEMFC

Although the nanometric scale information of CLs is limited, structural and compositional information does exist and it can be obtained before, during and after manufacturing the electrodes. Design parameters that are used and controlled before MEA's manufacturing typically include: (1) platinum load (γ_{Pt}) in mg Pt cm^{-2}; (2) ionomer load (β_N) which is a relation of nafion® weight to total electrode weight and (3) platinum to carbon weight ratio (θ_{Pt}), which is characteristic of the catalytic material synthesis. From such information and from other physical properties of its components (densities), volume fractions of phases in CL can be calculated.

On the other hand, the solid phase volume (V_S) of any mixture is equal to the total sum of individual phase mass (m) divided by the density (ρ) of each i element in the mixture, Eq. (2):

$$V_S = \sum \frac{m_i}{\rho_i} \quad (2)$$

Using design parameters (γ_{Pt}, β_N, θ_{Pt}) in Eq. (2) gives the volume occupied by each primary element in the solid phase of the CL. Eqs. (3), (4) and (5) can be used to calculate platinum (V_{Pt}), carbon (V_C) and nafion (V_N) volume, respectively:

$$V_{Pt} = \frac{V_S}{[(\beta_N(1+\theta_{Pt})/\theta_{Pt}\,\rho_N(1-\beta_N) + (1/\rho_{Pt}) + (1/\theta_{Pt}\,\rho_C)]\rho_{Pt}} \quad (3)$$

$$V_C = \left(\frac{V_{Pt}\,\rho_{Pt}}{\theta_{Pt}\,\rho_C}\right) \quad (4)$$

$$V_N = \left(\frac{\beta_N(1+\theta_{Pt})(V_{Pt}\,\rho_{Pt})}{(1-\beta_N)\theta_{Pt}\,\rho_N}\right) \quad (5)$$

where ρ_{Pt}, ρ_C and ρ_N are platinum, carbon and nafion densities, respectively.

On the other hand, Eq. (6) relates the electrode total porosity (Φ_T) with the solid phase volume (V_S) and the electrodes total volume (V_T)

$$\Phi_T = 1 - \frac{V_S}{V_T} = 1 - \frac{\sum m_i/\rho_i}{V_T} \quad (6)$$

Other important structural information that can be obtained before manufacturing the CL is the Pt and the C particle sizes. Pt is typi-