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Pore network modeling: Application to multiphase transport inside the cathode catalyst layer of proton exchange membrane fuel cell

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ABSTRACT

A pore network modeling (PNM) approach is developed to study multiphase transport phenomena inside a porous structure representative of the Cathode Catalyst Layer (CCL) of Proton Exchange Membrane Fuel Cells. Two algorithms for predicting the invasion of the CCL by liquid water are proposed and compared. The effect of wetting is studied and a change in wettability, from hydrophilic to hydrophobic, is shown to have a significant influence. The total liquid saturation at the end of invasion is lower when the network is hydrophilic whereas the number of breakthrough points is greater. The simulations fully support the idea that water exits the CCL through a series of independent outlet points. Diffusion processes in the gas phase are also analyzed within the framework of the PNM. The results indicate that the Knudsen effect, and to a lesser extent the diffusion-slip effect must be taken into account. These results open up the route for the development of a full coupled PN model of transport phenomena occurring in the CCL.

1. Introduction

Fuel cell is one of the most promising solutions for electrical energy production with no pollution emission. PEMFC (Proton Exchange Membrane Fuel Cell) is considered as an alternative to classical combustion engine for transport application. Nevertheless, before this technology enters into industrialization phase, some bottlenecks are to be solved, especially to reduce its cost and to increase its durability.

Fluid transfer, and especially water management [1–8] and references therein is a key factor on performance (flooding and drying), durability (reversible and non-reversible degradation mechanisms) but also cost (optimization of gas access to the reaction sites). These transfers (one-phase and/or two-phase) are closely linked to the structure (thickness, pore size distribution...) of the gas diffusion and active layers of the PEMFC as well as to their transport properties (protons, electrons, heat and mass).

In order to increase durability and reduce cost of PEMFC, the current components are to be improved but up to now the link between their local properties and their performance is not clearly understood (e.g. for instance [9]) so real improvements are based on empirical approaches which are limited as physical mechanisms inside fuel cells are complex and highly coupled. Another difficulty is linked to the scales of the components (from some nm for catalyst up to 100 cm^2 for the cell size with many intermediate scales such as 10–1000 nm (respectively 0.1–1 μm) for the pores of the active layer (resp. gas diffusion layer), 5–10 μm (respectively 100–300 μm) for the thickness of the active layer (resp. gas diffusion layer)... Fuel cells are then highly non-linear multiscale and multiphysics systems. Models coupling relevant phenomena can then help understanding the link between local properties of components and performance of PEMFC. This would also enable proposing improvements of components.

Modeling of PEMFC has been widely developing for the last years and review is beyond the scope of this paper (e.g. for instance [4,10]). Although different types of models can be found in the literature, macro-homogeneous modeling is the most commonly used especially in current performance models of PEMFC e.g. for instance [2,3,12–16]. In that case transfers are based on the classical Darcy law which is quite easy to use but requires the knowledge of the effective properties (conductivity, capillary pressure...) of the materials. Measurement of effective properties is still a challenge especially in the case of active layers (thin, not self-supported...) and so reliable model inputs are difficult to get. These effective properties remain for the moment badly known, especially when liquid water is present in the layers. Another drawback is that no local property of materials is really explicit in these effective properties so this approach cannot be used to propose reliable improvement of materials.

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Complementary approaches have been developed that allow taking into account some local structural properties of active layers. The first idea relates to the agglomerate model [3,15,10,17–21] which describes the active layers as a porous medium made of agglomerates (typical size 100–1000 nm) each of them made of several C/Pt (typical size 30 nm). This is consistent with SEM observations showing double pore size distribution (inside agglomerates and between agglomerates). Heat, mass and charge transfers at agglomerate scale (inside agglomerates) are calculated analytically using different assumptions (spherical agglomerates, electrical potential and temperature distribution...) [3,4,10,22,23]. This approach is sometimes implemented in macro-homogeneous performance models to take into account transfers at agglomerate scale. They allow for instance analyzing to a certain extent the influence of agglomerate size, electrolyte thickness around agglomerate, and component loadings on performance [15,16,21]. Fluid transfers between agglomerates are in that case based on averaged approach with a classical modeling (Darcy).

The second complementary idea is then to develop local approaches to analyze transfers between agglomerates, that is in the "large" (referred to also as "secondary") pore network formed by the voids existing between the agglomerates. Such models have appeared more recently [23,25,26] and allow very interesting discussion on the influence of structure of CCL on porosity, proton conductivity and gas diffusion for instance but they are for the moment limited to one-phase working conditions. This leads to a difficulty to analyze flooding of Cathode Catalyst Layer (CCL) which is considered as a key limitation to performance of PEMFC [8,21]. Even if the analysis of flooding in CCL remains up to now a challenge [4,5], one scenario is linked to the blockage of secondary pores (between agglomerates) by liquid water, enabling gas access to the catalyst sites in the agglomerates. So it appears interesting to study two-phase flows between agglomerates of a CCL. This can help understanding flooding of CCL and defining which properties of materials could limit this flooding.

As first step for this, the aim of the present work is to propose a way to model two-phase transfers between agglomerates of a CCL. It is based on Pore network modeling (PNM). PNM is well adapted for computing two-phase transport in porous media e.g. for instance [27] and allow linking its local properties to its transport effective properties. Widely used for soil application [28,29] PNM has been more recently applied to study liquid water transport inside the Gas Diffusion Layer (GDL) of PEMFC e.g. for instance [26,30–38]. In that case liquid water is supposed to invade the network from one side describing liquid invasion from the CCL into the GDL. Despite numerous assumptions (no condensation, no real interface coupling between the layers, most of time uniform injection...), PNM demonstrated its capability to analyze two-phase transport inside the GDL as a function of structure and local wettability. It also helped [26,30–38] understanding the role of wettability and of injection points, the formation of breakthrough points and the appearance of droplets at the interface between GDL and gas channels. It also enabled first links between hydrophobicity loss due to degradation and gas diffusion decrease over time in GDL [36].

The situation of CCL is more complex than the one of GDL even if we consider in this paper only transfers in the large pore network between agglomerates and not transfers inside agglomerates or through the electrolyte. Water is produced inside the CCL and the simulation of water production, water and gas transport in the CCL requires the consideration of full coupling between all these transfers as well as with the electro-chemical reactions within the CCL. Such a fully and highly complex coupled model is, however, beyond the scope of the present paper. Here, as a first step toward the complete CCL PN Model, we present and discuss two important aspects of the modeling in this prospect. The first one concerns the modeling of CCL water invasion resulting from water production within the CCL. For simplicity, the water production rates are considered as input parameters in this first approach. The second aspect concerns the modeling of diffusive transport in the gas phase. In addition to new insights into the invasion process of water from multiple sources randomly distributed within the CCL and the impact of wettability on the invasion process, two water invasion algorithms are tested and compared in the present study and it is found that the more complex one, referred to as the kinetic algorithm below, is more adequate. In the same spirit, the comparison between three models of diffusion transport in the gas phase, is helpful in the prospect of selecting the most appropriate model for developing the full coupled model mentioned before.

The paper is organized as follows. Section 2 describes the PNM. Two algorithms (sequential and kinetic) used to simulate liquid water invasion in the CCL are presented in Section 3. Comparison of the two algorithms is performed in Section 4 from the analysis of the fraction of breakthrough points at the outlet (CCL/GDL interface) and the overall saturation at the end of water invasion as a function of the fraction of active agglomerates in the system. Gas diffusion modeling is presented and discussed in Section 5.

2. PNM model

The CCL is assumed to be made of spherical agglomerates of carbon support and platinum particles. As sketched in Fig. 1, these agglomerates are surrounded by a thin film of Nafion® and they form a porous medium with "large" pores (free space between the agglomerates, also known as secondary pores) and small pores (free space inside the agglomerates, also known as primary pores).

In this work, we concentrate on the transfers within the pore space formed by the "large" pores (the inter-agglomerate pore space). As sketched in Fig. 2, this pore space is conceptualized as a network of pores connected by throats. A pore is represented by a sphere and a connecting throat by a cylindrical tube. Simple square (in 2D) and cubic (in 3D) networks are considered. Thus, each pore is connected to 4 neighbor pores in a 2D network and to 6 neighbor pores in a 3D network. As can be seen from Fig. 2, a throat is connected to 2 adjacent pores. The disordered nature of the inter-agglomerate pore space is taken into account through the "pore" size distribution (PSD), which is an input data of the model. This means that the diameter d_t of each throat is randomly distributed according to the considered PSD (note here that the measurement of PSD, generally by Hg porosimetry, is in fact more representative of diameters of throats than of pores). The diameter d_p of each pore is chosen to be equal or higher than the diameter of the largest throat connected to it: $d_p = \max(d_t) + \Delta d$, where Δd is a constant input parameter of the model. The distance a between the centers of two neighbor pores is called the network (or lattice) spacing and

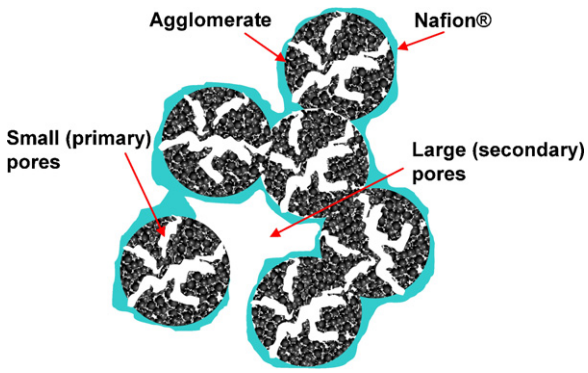

Fig. 1. Schematic of agglomerates and pores in a CCL.