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Modeling of the anode of a liquid-feed DMFC: Inhomogeneous compression effects and two-phase transport phenomena

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HIGHLIGHTS

- An isothermal two-phase across-the-channel model for liquid-feed DMFCs is presented.
- The model considers inhomogeneous compression of the GDL (non-uniform porosity).
- Effective anisotropic properties of the GDL are evaluated from empirical data.
- The hydrophobic Leverett J-function approach provides physically inconsistent results.
- Empirical $p_c - s$ data reflecting the mixed-wettability of GDLs give much better predictions.

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ABSTRACT

An isothermal two-phase 2D/1D across-the-channel model for the anode of a liquid-feed Direct Methanol Fuel Cell (DMFC) is presented. The model takes into account the effects of the inhomogeneous assembly compression of the Gas Diffusion Layer (GDL), including the spatial variations of porosity, diffusivity, permeability, capillary pressure, and electrical conductivity. The effective anisotropic properties of the GDL are evaluated from empirical data reported in the literature corresponding to Toray carbon paper TGP-H series. Multiphase transport is modeled according to the classical theory of porous media (two-fluid model), considering the effect of non-equilibrium evaporation and condensation of methanol and water. The numerical results evidence that the hydrophobic Leverett J-function approach is physically inconsistent to describe capillary transport in the anode of a DMFC when assembly compression effects are considered. In contrast, more realistic results are obtained when GDL-specific capillary pressure curves reflecting the mixed-wettability characteristics of GDLs are taken into account. The gas coverage factor at the GDL/channel interface also exhibits a strong influence on the gas-void fraction distribution in the GDL, which in turn depends on the relative importance between the capillary resistance induced by the inhomogeneous compression, R_c ($\propto \partial p_c/\partial \varepsilon$), and the capillary diffusivity, $\overline{\mathbf{D}}_\mathbf{c}$ ($\propto \partial p_c/\partial s$).

1. Introduction

The development of liquid-feed Direct Methanol Fuel Cells (DMFCs), a variant of hydrogen PEMFC technology in which the fuel is an aqueous methanol solution, has accelerated over the last years. Although the power densities that can be reached with PEMFCs are higher, liquid-feed DMFCs present two major advantages compared with PEMFCs: the easier delivery and storage of liquid methanol solutions, and the higher volumetric energy density of liquid methanol [1–3]. These characteristics make DMFCs a promising candidate as a power source for portable electronic applications, including cell phones, laptop computers, military equipment, etc. [4,5].

However, widespread commercialization of DMFCs is still hindered by several technological problems, such as the slow kinetics of the Methanol Oxidation Reaction (MOR) at the anode Catalyst Layer (CL) and the cathode mixed potential associated with the oxidation of methanol that crosses over the polymer membrane from anode to cathode [6]. Furthermore, the interplay between mass/charge/heat transport, electrochemical kinetics, inhomogeneous compression effects, interfacial contact resistances, and two-phase transport phenomena makes it difficult to achieve optimum design and operating conditions [7]. Thorough study of these

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complex and interrelated phenomena is therefore necessary from both the experimental and the modeling points of view [8].

One key element affecting fuel cell performance is the Gas Diffusion Layer (GDL). It provides several functions: a pathway for reactant access and excess product removal to/from the CLs, high electrical and thermal conductivity, and adequate mechanical support. In order to fulfill these requirements, GDLs are typically made of porous carbon paper or woven cloth [9]. Both media are characterized by exhibiting significant structural anisotropy due to the preferential orientation of carbon fibers, which typically results in different transport properties along the in-plane and through-plane directions [10]. In addition, the high porosity of these materials provides to the GDL a characteristic soft and flexible structure, susceptible of large deformations when subjected to compression [11]. This introduces important variations in the effective transport properties between the regions under the channel and under the rib when the fuel cell is assembled [8,12,–15].

Even though the fundamental role of the GDL has long been recognized by the fuel cell community [16–18], most models presented in the literature to date assume homogenous and isotropic GDL properties. However, this situation has changed during the last few years, and a larger effort is now devoted to the development of more comprehensive models reflecting the real characteristics and operating conditions of the GDLs [19]. Thus, different aspects such as the inhomogeneities caused by the assembly compression and manufacturing process, as well as the inherent anisotropy of the GDL, have been recently incorporated into numerical models. In addition, numerous experimental and numerical works exploring the effective transport properties of GDLs are now available in the literature [20]. This trend should be reinforced in the near future.

The influence of GDL inhomogeneities and anisotropic properties on PEMFC operation has been explored in several modeling works [21–25]. However, these phenomena have been traditionally ignored in DMFC modeling studies (see, e.g., [5,26,27] and references therein), and only a few works can be found in the open literature. Möst et al. [28] presented an analysis of the diffusive mass transport in the anode GDL of a DMFC. In this work, the anisotropic dry diffusivities of different GDLs at various compression ratios were measured, and subsequently employed in Monte Carlo simulations taking into account inhomogeneous compression effects. The limiting current densities predicted by this single-phase model were in qualitative agreement with those obtained experimentally, but a systematic overestimation was observed. Miao et al. [29] developed a two-phase 2D across-the-channel model of a DMFC to investigate the effects of GDL anisotropic properties, inhomogeneous compression, and electrical and thermal contact resistances. These phenomena were taken into account by considering the empirical data reported by Himanen et al. [8,13–15] as a function of the in-plane coordinate x. They concluded that the anisotropy of the GDL has a significant effect on the distribution of species concentration, overpotential, current density, and temperature; even though the isotropic and anisotropic models lead to very similar polarization curves. They also observed that the electrical contact resistance at the CL interface and the GDL compression both play an important role in determining cell performance. In a subsequent work, Miao et al. [30] presented an upgraded version of this model, in which anisotropic heat transfer coefficients were used to capture a more realistic heat transport mechanism. This study was exclusively focused on the influence of GDL anisotropic properties, inhomogeneous compression and contact resistances on heat generation and transport processes. They found that these phenomena have a strong impact on heat transfer processes in DMFCs. Using a model similar to that presented in Ref. [29], He et al. [31] investigated the behavior of water transport through the MEA. The numerical results showed that both the channel-rib pattern and the deformation of the GDL can cause an uneven distribution of the water-crossover flux along the in-plane direction. In addition, they concluded that both the contact angle and the permeability of the cathode GDL can significantly influence the water-crossover flux.

The effect of assembly compression on the performance of both active and passive DMFCs has been also stressed in a few experimental works [32,33]. Even though the number of studies related to DMFCs is notably lower compared to those available for PEMFCs [32,34–37], these results are far enough to visualize the importance of assembly pressure on DMFC operation. Nevertheless, it would be interesting to explore a wider range of operating conditions and MEA configurations (particularly different type and thicknesses of the GDL) in future experimental work.

The above literature review shows the large impact that GDL inhomogeneous compression and anisotropic properties have on mass/charge/heat transport in DMFCs, thereby affecting fuel cell performance and lifetime. These phenomena should be investigated by physically sound mathematical models including detailed descriptions of the transport processes that occur in the GDL [27].

The present work presents an isothermal two-phase 2D/1D across-the-channel model for the anode of a liquid-feed DMFC. The model takes into account the spatial variations induced by the inhomogeneous assembly compression of the GDL, as well as the inherent anisotropic properties of this key element of the cell. The assembly process is simulated by a novel Finite Element Method (FEM) model, which fully incorporates the nonlinear orthotropic mechanical properties of the GDL (Toray® carbon paper TGP-H series) [11]. The resulting porosity distribution is then used to evaluate the effective transport properties of the GDL, i.e., mass diffusivity, permeability, capillary pressure and electrical conductivity, through empirical data reported in the literature. Conceived as an extension of our previous research activity on DMFCs [6], the present model brings new light on the potential influence of GDL inhomogeneous compression on capillary transport processes and gas saturation distribution in the anode of liquid-feed DMFCs. In its present form, the 2D/1D across-the-channel model constitutes a first step towards the development of a full 3D-model for DMFCs that properly takes into account the influence of inhomogeneous compression effects on multiphase transport phenomena.

2. Numerical model

The 2D/1D DMFC model presented in this work is based on the 3D/1D single-phase model previously proposed by Vera [6]. The 3D geometry of the anode has been reduced to a 2D across-the-channel GDL section, while the single-phase 1D model, comprising the catalyst layers, the membrane, and the cathode GDL, presents only minor changes with respect to that presented in Ref. [6]. As major improvements, the upgraded 2D anode model takes into account multiphase transport phenomena according to the classical theory of porous media (two-fluid model), retaining the effect of non-equilibrium phase change of methanol/water. It also includes the effects of the inhomogeneous compression of the GDL, incorporated through the non-uniform porosity distribution obtained from a previous analysis of the GDL compression process [11]. Specifically, the model makes extensive use of empirical correlations of anisotropic carbon paper-based GDLs to evaluate the resulting non-uniform diffusivity, permeability, capillary pressure and electrical conductivity fields induced by the assembly pressure. Finally, the GDL electronic potential is now solved, with the possibility of including the effect of non-uniform contact resistances at the GDL/Rib and GDL/CL interfaces as boundary conditions. The main contribution of this work is to explore the potential impact of GDL inhomogeneous assembly compression on two-phase capillary transport in the anode of a DMFC. The mathematical formulation of