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On the effect of operating conditions in liquid-feed Direct Methanol Fuel Cells: A multiphysics modeling approach

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Abstract

A multiphysics model for liquid-feed Direct Methanol Fuel Cells is presented. The model accounts for two-dimensional (2D) across-the-channel anisotropic mass and charge transport in the anode/cathode Gas Diffusion Layers (GDLs), including the effect of GDL assembly compression and electrical contact resistances at the Bipolar Plate (BPP) and membrane interfaces. A one-dimensional (1D) across-the-membrane model is used to describe local species diffusion through the microporous layers, methanol/water crossover, proton transport, and electrochemical reactions, thereby coupling both GDL sub-models. The 2D/1D model is extended to the third dimension and supplemented with 1D descriptions of the flow channels to yield a 3D/1D + 1D model that is successfully validated. A parametric study is then conducted on the 2D/1D model to examine the effect of operating conditions on cell performance. The results show that an optimum methanol concentration exists that maximizes power output due to the trade-off between anode polarization and cathode mixed overpotential. For fixed methanol concentration, cell performance is largely affected by the oxygen supply rate, cell temperature, and liquid/gas saturation levels. There is also an optimal GDL compression due to the trade-off between ohmic and concentration losses, which strongly depends on BPP material and, more weakly, on the actual operating conditions.

Keywords: DMFC, GDL compression, multiphysics modeling, operating conditions, parametric study

1. Introduction

Polymer Electrolyte Membrane Fuel Cells (PEMFCs) are promising candidates to replace today's fossil-based power sources, enabling a sustainable and efficient electrochemical generation of power by the direct conversion of the chemical energy stored in a fuel into electricity. Despite the major interest of the automotive industry on high-performance hydrogen PEMFCs, liquid-feed Direct Methanol Fuel Cells (DMFCs) are best suited for portable electronic devices with small power requirements due to the higher energy density and the ease of handling and storage of liquid alcohols [1, 2].

The heart of a DMFC is the so-called Membrane Electrode Assembly (MEA). The basic structure of the MEA is composed of five layers: a central Proton Exchange Membrane (PEM), usually made of Nafion[®], which allows the transport of protons and avoids the mixing of reactants [3, 4]; anode and cathode Catalyst Layers (CLs), where the electrochemical reactions take place catalyzed by noble metals (typically Pt-Ru at the anode and Pt at the cathode) [5]; and two porous carbon-paper or carbon-cloth Gas Diffusion Layers (GDLs), which provide passage for reactant access

and product removal to and from the catalyst layers, electrical and thermal conductivity, and adequate mechanical support to the membrane [6–9]. The MEA is further assembled between two Bipolar Plates (BPPs), usually made of graphite or metal, which supply the methanol solution and the oxidizer flow (air or pure oxygen) and evacuate the reaction products (carbon dioxide at the anode and water at the cathode) through the flow channels grooved on them, collect the electric current through the ribs between the channels, remove generated heat, and provide structural integrity to the system [10].

However, liquid-feed DMFCs suffer from various technological drawbacks. The most serious ones are the sluggish kinetics of methanol electrooxidation at the anode, and the mixed overpotential induced by methanol crossover at the cathode [11–23]. In addition, the inadequate evacuation of carbon dioxide from the anode compartment, combined with heat and water management issues, such as cathode flooding, still pose serious problems to commercialization [24–30]. A wide variety of strategies have been adopted to overcome these difficulties. These include the addition of PTFE-based Microporous Layers (MPLs) onto the GDL face adjacent to the catalyst layers to reduce water/methanol crossover and improve water management at the cathode [31–35], the creation of more active multifunctional catalysts [36–38], the development of new membranes with reduced crossover rates and higher durability [39–41], and the design of flow fields with enhanced mass-transfer characteristics [42, 43].

In this context, the combination of detailed experimental research with advanced mathematical modeling emerges as an essential tool to improve our understanding of the complex and interrelated transport phenomena that occur inside liquid-feed DMFCs. The development of predictive models to describe and optimize the performance and efficiency of DMFCs has motivated a large body of work during the last decade [44], including several numerical studies that explore the effect of design and operational parameters, such as flow field geometry, MEA configuration, reactant concentrations and flow rates, cell temperature, two-phase working conditions, GDL assembly compression, etc.

In electrochemistry, the Tafel equation relates the rate of an electrochemical reaction, measured by the current density i , with the applied overpotential η via a linear correlation of the form $\eta = a + b \log i$, where the coefficients a and b can be measured experimentally. In elementary electrochemical reactions, the measured Tafel slope b is a well-defined constant that is inversely proportional to the charge transfer coefficient. However, in multi-step electrocatalytic reactions, such as the electrooxidation of methanol, b may be potential-dependent due to the changes of the reaction mechanism associated with the change in reaction conditions (surface intermediates, coverage factors, etc.) induced by the electrical potential [45]. The latter case is often referred to as non-Tafel kinetics in DMFC modeling studies.

Meyers & Newman [46–48] developed a 1D isothermal single-phase model for the MEA of a liquid-feed DMFC, establishing a theoretical framework for the description of the multi-step Methanol Oxidation Reaction (MOR) coupled to mass and charge transport processes in multicomponent membranes. They investigated the non-Tafel MOR kinetics on Pt-Ru catalysts based on the series of elementary steps described by Gasteiger et al. [49]. The proposed model was able to capture the well-known transition from zero-order kinetics at high methanol concentrations to first-order kinetics at low methanol concentrations. Argyropoulos et al. [50] developed a semi-empirical model to describe DMFC

performance by combining Tafel-like kinetics for both methanol oxidation and oxygen reduction with experimentally measured effective mass transport coefficients. They found good agreement with polarization curves obtained in a cell fixture equipped with parallel flow fields over a wide range of operating conditions.

Wang & Wang [51] proposed a comprehensive 2D-along-the-channel MEA + 1D channel isothermal two-phase model based on the multiphase mixture (M^2) formulation [52]. The model considered liquid and gas phases to be in thermodynamic equilibrium, and accounted for the cathode mixed overpotential due to methanol crossover by diffusion, convection, and electroosmotic drag. They also incorporated an abrupt transition from zero- to first-order MOR kinetics at methanol concentrations below 0.1 M. Murgia et al. [53] developed a 1D isothermal two-phase model based on phenomenological transport equations for the various components of the MEA. The model assumed electrochemical kinetics to be described by Butler-Volmer equations, and included empirical relations to model non-equilibrium phase change phenomena and capillary transport of liquid water in the cathode compartment. Divisek et al. [54] presented a 2D across-the channel non-isothermal two-phase model, considering a multi-step kinetic mechanism for both the methanol oxidation and the oxygen reduction reactions. Their model took into account the coexistence of hydrophilic and hydrophobic pores in the GDL using a novel expression to relate capillary pressure and liquid saturation.

More recently, Ge & Liu [55] presented a 3D isothermal single-phase model with Tafel kinetics to analyze the effects of operating conditions and MEA properties on cell performance and methanol crossover. Vera [56] developed a 3D isothermal single-phase model for the anode of a liquid-feed DMFC, which was locally coupled at the anode GDL/CL interface to a semi-analytical 1D model describing the membrane, catalyst layers and cathode GDL. Vera's 1D model was based on the model previously proposed by García et al. [57]. Both works [56] and [57] incorporated the effect of non-Tafel MOR kinetics according to the original model presented by Meyers & Newman [46–48]. Liu & Wang [58] developed a fully 3D isothermal M^2 model based on the formulation of Wang & Wang [51] to explore mass transport phenomena and the interplay between local current density and methanol crossover on DMFC operation. Yang et al. [59] reported a 3D MEA + 1D channel isothermal two-fluid model incorporating the effect of non-equilibrium evaporation/condensation of methanol and water, and the zero- to first-order MOR transition. Casalegno et al. [60] presented a 1D across-the-channel + 1D channel isothermal model, considering two-phase transport at the anode, thermodynamic equilibrium between phases, and Tafel kinetics. The predictive capabilities of the calibrated model were extensively validated against experimental polarization curves and crossover data. Oliveira et al. [61] developed a 1D across-the-channel non-isothermal single-phase model with non-Tafel kinetics to study the effect of methanol and water crossover. Ko et al. [62] presented a 1D across-the-channel isothermal two-phase model, considering methanol to be in thermodynamic equilibrium and water only in liquid phase. They also adopted the kinetics of Meyers & Newman [46–48] to model the MOR. Finally, Miao et al. [63] reported a 2D across-the-channel non-isothermal two-phase model to investigate the effects of GDL anisotropic transport properties, inhomogeneous assembly compression, and electrical/thermal contact resistances. Their formulation included detailed multi-step kinetics for methanol oxidation, and Tafel kinetics for oxygen

reduction.

In addition to these works, many numerical, analytical, semi-analytical, and semi-empirical models, formulated either for single-phase or two-phase conditions, have provided fundamental information on the operation and performance of liquid-feed DMFCs (see, e.g, [64–90] and references therein). A close inspection of the literature cited so far shows that future research should be oriented towards the development of comprehensive multiphysics models including accurate descriptions of effective transport properties and two-phase phenomena, as well as detailed electrochemical kinetics [44]. The recent progress achieved in in-operando visualization and diagnostic tools [30, 91–94], and in the characterization of transport and mechanical properties of fuel cell components [6–9, 95–97], opens new horizons towards this goal and motivates new modeling exercises.

This work presents a detailed study of the intertwined effects of operating conditions on the performance of liquid-feed DMFCs. To this end, the multiphysics 2D/1D across-the-channel model developed by the authors in previous works [86, 89, 97] is upgraded to account for (i) multiphase transport at the cathode, (ii) the effect of electrical contact resistance between the GDL-MPL diffusion media and the catalyst-coated membrane, and (iii) the spontaneous hydrogen evolution that occurs at the anode catalyst layer under oxygen-starved conditions. The organization of the paper is as follows. The mathematical formulation of the 2D/1D across-the-channel model is presented in Section 2, together with the geometrical parameters and the cases under study. The model is then extended to the third dimension in Section 3, where it is also combined with 1D descriptions of the anode and cathode channels to yield an advanced 3D/1D MEA + 1D channel model, which is successfully validated against previous experimental and numerical results. A parametric study conducted over the 2D/1D model is presented in Section 4, including detailed discussions on the combined effects of reactant concentrations, GDL compression, cell temperature, and gas/liquid saturation levels at the anode/cathode channel interfaces. Finally, the concluding remarks are given in Section 5.

2. Numerical model

The present 2D/1D across-the-channel model is an extension of the models reported by the authors in [86, 89, 97]. The upgraded formulation presented here incorporates a 2D multiphase description of the cathode compartment, instead of the 1D single-phase approach that had been assumed so far. In addition, the model incorporates the effect of electrical contact resistances between the GDL-MPL diffusion medium and the membrane, as well as the hydrogen evolution kinetics in the anode electrode to provide a better electrochemical description at low oxygen concentrations. The model setup is divided into two successive steps. First, the GDL assembly process is simulated using the ABAQUS[®] finite element model by García-Salaberri et al. [97]. The compressed domains and porosity distributions, $\varepsilon(x, y)$, of the anode and cathode GDLs, as well as the contact pressure profiles at the GDL/BPP interface, $p_c^{\text{gdl/bpp}}(x)$, and at the lower interface between the diffusion medium and the membrane, $p_c^{\text{gdl/mem}}(x)$, are then imported into the CFD code ANSYS[®] FLUENT, where the DMFC model is implemented. Examples of GDL porosity distributions and interfacial contact

pressure profiles can be found elsewhere [97].

The proposed multiphysics model accounts for the effect of non-uniform porosity on GDL mass and charge effective transport properties (i.e., electrical conductivity, $\bar{\sigma}^{\text{eff}}$, diffusivity, $\bar{D}^{\text{eff}}$, permeability, $\bar{K}$, and capillary diffusivity, $\bar{D}_c$, tensors), and of electrical contact resistances at the GDL/BPP interface, $R_c^{\text{gdl/bpp}}(p_c^{\text{gdl/bpp}})$, and between the GDL-MPL diffusion medium and the membrane, $R_c^{\text{gdl/mem}}(p_c^{\text{gdl/mem}})$. All effective mass and charge transport properties of the GDL used in the model are evaluated in terms of local porosity from empirical correlations corresponding to anisotropic Toray[®] carbon paper [86, 89, 97]. The mathematical formulation of the 2D/1D DMFC model and the physicochemical and transport properties involved are presented in Appendix A; further details on the implementation and the underlying hypothesis of the numerical model can be found elsewhere [86, 89, 97]. The main features of the current version of the 2D/1D across-the-channel model, including the computational domain considered here, are described below.

As depicted in Fig. 1, the computational domain incorporates the seven layers typically found in the MEA: the five basic layers comprising the anode and cathode GDLs (agdl/cgdl), the anode and cathode catalyst layers (acl/ccl), and the membrane (mem), plus two additional microporous layers (ampl/cmpl) placed between the GDLs and the catalyst layers. The numerical model is split in three different domains: two 2D domains corresponding to the anode and cathode GDLs (delimited by blue and red solid lines in Fig. 1, respectively), and a 1D domain including the membrane, microporous layers, and catalyst layers (delimited by a green dashed line in Fig. 1). The GDL domains incorporate full 2D description of mass, momentum, species, and charge transport, while the 1D domain provides a local description of through-plane transport processes in the remaining components of the MEA. Specifically, the 1D model accounts for mass transport of methanol and oxygen in the microporous layers, methanol/water crossover and proton transport through the membrane, and the electrochemical reactions at the catalyst layers. Both GDL models are locally coupled to the 1D model at each computational face of the anode and cathode GDL/MPL interfaces. Figure 1 also shows the electrochemical reactions incorporated into the model, i.e., the MOR and Hydrogen Evolution Reaction (HER) at the anode catalyst layer, and the Oxygen Reduction Reaction (ORR) and MOR induced by methanol crossover at the cathode catalyst layer. Nearly zero methanol concentration is assumed at the cathode catalyst layer (i.e., $C_{\text{ml,ccl}} \simeq 0$, $i_{\text{MOR,c}} = i_p \simeq 6FN_{\text{ml,cross}}$) due to the high overpotentials for the electrooxidation of methanol in that electrode (see, e.g., [51, 56, 57, 60, 78]). The HER becomes relevant both at open circuit ($I \rightarrow 0$), and when the Tafel exponential of the inverse reaction ($i_{\text{HER}} \propto \exp(-\eta_a)$) ceases to be negligible at very small anode overpotentials ($\eta_a \rightarrow 0$) under oxygen-starved conditions (large η_c); HER kinetics is modeled according to the formulation recently introduced by Ye et al. [79] and Yang et al. [84].

2.1. Geometry and case studies

For simplicity in the presentation, this work assumes a parallel channel configuration. Therefore, the computational domain (delimited by a black solid line in Fig. 1) is restricted to the region comprised between the mid-plane of a channel and that of the neighboring rib, with symmetry conditions prescribed at both boundaries. The geometrical dimensions

are kept constant throughout the study, except for the validation campaign performed in Section 3 using the extended 3D/1D MEA + 1D channel model. The four geometrical parameters that define both 2D anode and cathode GDL models, i.e., rib half-width (w_{rib}), uncompressed GDL thickness ($\delta_{\text{agdl}}^u, \delta_{\text{cgdl}}^u$), distance between rib and channel symmetry planes (w_{gdl}), and rib fillet radius (r_{rib}), are listed in Table 1, along with the thicknesses (δ_i) of the different layers that make up the 1D model. Also included is the initial uncompressed porosity of the GDLs ($\varepsilon_{\text{agdl}}^u, \varepsilon_{\text{cgdl}}^u$).

The aim of this work is to present a parametric study covering all operational parameters involved in the 2D/1D model (see Fig. 1). In comparison to a fully 3D model, the lower computational cost of the 2D/1D model enabled the computation of a large number of polarization curves and the associated solution variables reported in this work. The analysis includes the effect of oxygen, $C_{\text{O}_2}^{\text{ch}}$, and methanol, $C_{\text{ml}}^{\text{ch}}$, concentrations at the GDL/channel interface, GDL compression ratio, $\text{CR} = (\delta_{\text{gdl}}^u - \delta_{\text{gdl}}^c)/\delta_{\text{gdl}}^u$, electrical contact resistance at the GDL/BPP interface, $R_c^{\text{gdl/bpp}}$, and between the GDL-MPL diffusion medium and the membrane, $R_c^{\text{gdl/mem}}$, cell temperature, T , and anode/cathode gas/liquid saturation levels, $1 - s_a^{\text{ch}}$ and s_c^{ch} . The variation of the GDL/BPP electrical contact resistance with interfacial contact pressure is modeled for two different BPP materials: graphite, $R_c^{\text{gdl/bpp}} = 2(p_c^{\text{gdl/bpp}})^{-0.8} \text{ m}\Omega \text{ cm}^2$, and stainless steel (or metallic), $R_c^{\text{gdl/bpp}} = 186(p_c^{\text{gdl/bpp}})^{-1.09} \text{ m}\Omega \text{ cm}^2$, characterized by low and high electrical contact resistances, respectively [89]. The influence of the electrical contact resistance between the diffusion medium and the membrane, $R_c^{\text{gdl/mem}}$, has been examined separately in one section, being neglected in the rest of the work, due to the large uncertainty concerning its value, with variations of more than one order of magnitude between authors [63, 99–102]. In first approximation, $R_c^{\text{gdl/mem}}$ is modeled using a correlation similar to that for graphite BPPs, $R_c^{\text{gdl/mem}} = 2\Pi(p_c^{\text{gdl/mem}})^{-0.8} \text{ m}\Omega \text{ cm}^2$, except for the presence of a constant multiplicative factor Π that is freely varied.

Table 2 summarizes the operating conditions analyzed in the parametric study, in which both the liquid-phase pressure at the anode, $p_{\text{a,l}}^{\text{ch}}$, and the gas-phase pressure at the cathode, $p_{\text{c,g}}^{\text{ch}}$, are kept equal to 1 bar. It should be noted that the range of oxygen concentrations ($C_{\text{O}_2}^{\text{ch}} = 2 - 6 \text{ mol/m}^3$) is representative of the conditions found at the GDL/channel interface in active air-feed DMFCs operated at ambient pressure, where the consumption of oxygen along the channel and the mass-transfer resistance between the channel and the GDL reduces the oxygen concentration at the GDL/channel interface below the inlet value ($\bar{C}_{\text{O}_2}^{\text{ch,in}} \simeq 7 \text{ mol/m}^3$). This range also covers the rather small oxygen concentrations found at the GDL/channel interface of passive-feed DMFCs.

For reference purposes, the concentration of oxygen at the GDL/channel interface, $C_{\text{O}_2}^{\text{ch}}$, can also be expressed in terms of the cathode stoichiometric ratio, ξ_c , corresponding to a cell with an average oxygen concentration in the cathode channel equal to the specified oxygen concentration, $\bar{C}_{\text{O}_2,\text{avg}}^{\text{ch}} = C_{\text{O}_2}^{\text{ch}}$ [62, 75]. From a global oxygen mass balance and the definition of stoichiometric ratio, we may write

$$\left. \begin{aligned} \bar{C}_{\text{O}_2}^{\text{ch,out}} &= \bar{C}_{\text{O}_2}^{\text{ch,in}} - \frac{I + I_p}{4F} \frac{A_{\text{cl}}}{Q_{\text{c,g}}^{\text{ch,in}}} \\ \xi_c &= \frac{4F Q_{\text{c,g}}^{\text{ch,in}} \bar{C}_{\text{O}_2}^{\text{ch,in}}}{(I + I_p) A_{\text{cl}}} \end{aligned} \right\} \Rightarrow \bar{C}_{\text{O}_2}^{\text{ch,out}} = \bar{C}_{\text{O}_2}^{\text{ch,in}} \left(1 - \frac{1}{\xi_c} \right) \quad (1)$$

where A_{cl} is the cell active area, and $\dot{Q}_{c,g}^{ch,in}$ is the air feed flow rate. Imposing now that the average oxygen concentration in the channel,

$$\bar{C}_{O_2,avg}^{ch} = \frac{\bar{C}_{O_2}^{ch,in} + \bar{C}_{O_2}^{ch,out}}{2} = \bar{C}_{O_2}^{ch,in} \left(1 - \frac{1}{2\xi_c}\right), \quad (2)$$

is equal to the specified oxygen concentration, $\bar{C}_{O_2,avg}^{ch} = C_{O_2}^{ch}$, the cathode stoichiometric ratio reduces to

$$\xi_c = \left[2 \left(1 - C_{O_2}^{ch} / \bar{C}_{O_2}^{ch,in}\right)\right]^{-1} \quad (3)$$

This estimative value of ξ_c corresponds to a cell operated at a (variable) reference current density $I_{ref} = I + I_p$ (i.e., variable feed flow rate), so that $\xi_c = 1$ when the outlet oxygen concentration, $\bar{C}_{O_2}^{ch,out}$, vanishes.

3. Model validation: 3D/1D MEA + 1D channel model

Before proceeding with the parametric study, the predictive capabilities of the proposed 2D/1D across-the-channel model were validated against experimental and numerical results taken from the literature [16, 29, 59, 103]. These include polarization curves, limiting current density data, and along-the-channel spatial distributions of different variables. For the validation campaign, the 2D/1D across-the-channel MEA model was extruded in the third dimension and coupled to 1D descriptions of the flow channels to account for the downstream variation of methanol/oxygen concentration, gas/liquid saturations and pressures, and mass-transfer resistances at the GDL/channel interfaces. As depicted in Fig. 2, the 3D/1D MEA model was divided into a sufficiently large number of evenly-distributed stations (z -coordinate), which were locally coupled to the 1D channel models. The channel models were implemented in ANSYS® FLUENT in the form of user defined functions. In the iterative process, the mass fluxes computed by the 3D/1D MEA model at the GDL/channel interfaces were used to update the spatial distributions along the channels. The resulting local values of concentration, saturation, and pressure at the GDL/channel interfaces were subsequently imposed at each station of the 3D/1D MEA model to recalculate the solution in the next iteration, thereby closing the problem. A total of 20 stations were used in the simulations, since no significant changes were found using 40 stations. The 1D channel models were based on formulations previously reported by Wang & Wang [51], Yang et al. [59], and Yang & Zhao [70]. A drift-flux bubbly-slug model was used for the anode channel, whereas a homogenous mist-flow model was used for the cathode channel; the mathematical formulation of both models is presented in Appendix B. The governing equations for the 3D/1D MEA model coincide with those presented in Appendix A for the 2D/1D model, except for the fact that the formulation in the GDLs is fully 3D in (x, y, z) -space, and the variables in the local 1D across-the-membrane model vary not only with x , but also with z . The same GDL effective transport properties were used in the two orthogonal in-plane directions (x - and z -coordinates).

The first experimental dataset selected to validate the model was that reported by Lu & Wang [29], who examined the performance of a DMFC equipped with a Toray carbon-paper based MEA similar to the one considered here. Figure 3

compares the polarization curves obtained numerically with those reported by Lu & Wang [29] for 1 M and 2 M methanol solutions (the details of the simulations are given in the figure caption). It is seen that strong mass transport limitations arise at the anode for 1 M methanol, leading to a sharp drop of the cell voltage from about 0.35 V. For 2 M methanol, the cell performance is worse at high cell voltages due to methanol crossover, whereas the limiting current density is higher owing to the lesser impact of mass transport losses. The numerical calculations are in good overall agreement with the measured cell performance, but do not reproduce all the details. The deviations should be attributed to the uncertainty in the assumed geometry and operating conditions [29], and to the simplifying assumptions adopted in the mathematical model. In particular, the accurate modeling of the two-phase mass transport processes that occur at the GDL/channel interface remains an important challenge still to be solved.

Secondly, the predictive capabilities of the model were compared to the results reported in the experimental and numerical works of Xu et al. [16] and Yang et al. [59], respectively. An isotropic Bruggeman correction [104] was considered in this case for the GDL dry effective diffusivity, $f^{ip/tp} = \varepsilon^{1.5}$, due to the lower tortuosity of carbon-cloth GDLs [59, 105, 106]. The mass-transfer resistances at the GDL/channel interfaces were also set to zero, i.e., $h^{agdl/ch} = h^{cgdl/ch} \rightarrow \infty$ ($C_{ml}^{ch} = \bar{C}_{ml}^{ch}$, $C_{O_2}^{ch} = \bar{C}_{O_2}^{ch}$), as assumed by Yang et al. [59]. This hypothesis should be attributed to the improved gas removal characteristics at the GDL/channel interface observed in DMFCs equipped with carbon-cloth instead of carbon-paper GDLs [29, 105, 107]. Figure 4 shows the computed limiting current density as a function of methanol feed concentration, $\bar{C}_{ml}^{ch,in} = 0.125 - 0.75$ M, for various total methanol flow rates, $Q_{a,l}^{ch,in,T} = 1 - 25$ ml/min (see figure caption for details), whereas Fig. 5 shows along-the-channel distributions of methanol concentration, gas-void fraction, and current density at $V_{cell} = 0.25$ V corresponding to a 0.5 M methanol solution for the same range of flow rates. Good overall agreement is observed between the predicted numerical results and the experimental data of Xu et al. [16]. Under the high cathode stoichiometric conditions examined here [16, 59], the limiting current density increases almost linearly with the methanol feed concentration due to the larger availability of methanol at the anode catalyst layer. In addition, for a given methanol concentration the limiting current density increases with the methanol flow rate as a result of the more uniform distribution of methanol over the cell active area and the enhanced evacuation of carbon dioxide from the cell (see Fig. 5) [16, 59]. Similar conclusions were derived by Yang et al. [59] in their validation analysis against the experimental data of Xu et al. [16].

Thirdly, the model predictions were compared against the experimental observations of Sauer et al. [103], who confirmed the existence of the so-called bifunctional regime, in which liquid-feed DMFCs exhibit both galvanic (current-generating) and electrolytic (current-consuming) regions under oxygen-starved conditions. In the simulations, the GDL dry effective diffusivity was again modeled using the isotropic Bruggeman correction [104] to reproduce the diffusive properties of the carbon-cloth GDL employed in [103]. The mass-transfer coefficients at the GDL/channel interfaces were modeled as described in Appendix B. Figure 6 shows the computed along-the-channel oxygen and current density distributions for three different air flow rates, $Q_{c,g}^{ch,in} = 3, 5, \text{ and } 10$ ml/min, at approximately the same output current

density ($I \approx 20 \text{ mA/cm}^2$); the cell voltage is indicated between brackets. Good qualitative agreement is found between the numerical results and the experimental data of Sauer et al. [103]. As can be seen, at high air flow rates ($Q_{c,g}^{\text{ch,in}} = 10 \text{ ml/min}$) the oxygen supply rate is large enough to sustain the high parasitic current densities generated at the low output current density under consideration. In this case, the current density is positive and uniformly distributed over the entire cell active area. However, when the air flow rate is reduced ($Q_{c,g}^{\text{ch,in}} = 3$ and 5 ml/min) the amount of available oxygen becomes too small to sustain its parasitic consumption rate, and the oxygen supply is depleted at a certain downstream station. As a result, the cell starts to operate in a bifunctional regime. The oxygen-starved region works in electrolytic mode due to the spontaneous evolution of hydrogen through the hydrogen evolution reaction at the anode catalyst layer, which consumes a large fraction of the electrons generated in the oxygen-rich galvanic region. The extent of the electrolytic region increases as the air flow rate is reduced, accompanied by a strong decrease of the cell voltage [79, 84, 103, 108–110]. Further results of DMFCs operating in another bifunctional regime arising at the rib/channel scale will be presented in the next section.

In addition to the above results, a detailed validation of the model regarding the effects of GDL assembly compression and electrical contact resistances at the GDL/BPP interface was presented elsewhere [89]. The ability of the model to reproduce the experimentally observed trends in all the cases under study provides strong support to the multiphysics modeling approach adopted in this work.

4. Parametric study

This section presents a comprehensive parametric study covering the main operational parameters affecting DMFC performance. As previously discussed, the lower computational cost of the 2D/1D model enabled the computation of a substantial number of polarization curves (~ 750) and the associated solution variables to be discussed below.

4.1. Effect of methanol and oxygen concentrations

Figure 7 shows output power density, parasitic current density, and fuel utilization (FU) as a function of oxygen concentration, $C_{\text{O}_2}^{\text{ch}} = 2 - 5 \text{ mol/m}^3$, for $V_{\text{cell}} = 0.25 \text{ V}$ (close to maximum power density) and various methanol concentrations, $C_{\text{ml}}^{\text{ch}} = 1, 2$, and 3 M . Also shown are the polarization curves corresponding to these methanol solutions and three specified oxygen concentrations, $C_{\text{O}_2}^{\text{ch}} = 2, 3.5$, and 5 mol/m^3 ($\xi_c = 0.7, 1$, and 1.75 , respectively).

First, we shall discuss the influence of oxygen concentration on the power output. As seen in Figs. 7(a) and (c), the peak power density remains almost unaltered at 41 mW/cm^2 for $C_{\text{ml}}^{\text{ch}} = 1 \text{ M}$ when $C_{\text{O}_2}^{\text{ch}}$ is increased from 2 to 5 mol/m^3 , while it grows from 51 to 96 mW/cm^2 for $C_{\text{ml}}^{\text{ch}} = 2 \text{ M}$, and from 23 to 92 mW/cm^2 for $C_{\text{ml}}^{\text{ch}} = 3 \text{ M}$. The concentration of oxygen has little effect at small methanol concentrations ($C_{\text{ml}}^{\text{ch}} = 1 \text{ M}$) due to the strong mass transport losses caused by the low diffusivity of liquid methanol ($D_{\text{ml,water}}^{\text{bulk}}/D_{\text{O}_2,\text{air}}^{\text{bulk}} \sim \mathcal{O}(10^{-3} - 10^{-4})$), which results in low parasitic current densities (see Fig. 7(b)) [16, 19, 24, 56, 61]. In contrast, for higher methanol concentrations ($C_{\text{ml}}^{\text{ch}} = 2$ and 3 M) the cell shows a large sensitivity to oxygen concentration. On one hand, increasing the concentration of methanol reduces the anode

overpotential; but, on the other hand, it increases methanol crossover and therefore the cathode mixed overpotential (see, e.g., [11–22, 24, 51, 62, 72]). The performance loss caused by methanol crossover grows as the methanol concentration is increased and the oxygen concentration is reduced, which eventually gives rise to severe mass transport limitations at the cathode due to the strong parasitic consumption of oxygen [24, 51]. The trade-off between the aforementioned competing effects leads to an optimum methanol concentration that maximizes the power output of the cell [15, 21, 24, 51]. For the particular MEA considered here, the maximum power density is achieved for 2 M methanol in almost the entire range of oxygen concentrations. Note that the power density obtained with 3 M methanol becomes comparable to that reached with 2 M methanol only when the oxygen concentration is high enough so as to alleviate the strong detrimental effect caused by methanol crossover.

Turning now the attention to fuel utilization, Fig. 7(b) shows that it decreases systematically with the concentration of methanol, varying from almost full conversion (95%) for 1 M methanol, to medium conversion (60 – 80%) for 2 M, and low conversion (25 – 55%) for 3 M. As previously discussed, this effect is caused by the increase of unreacted methanol at the anode catalyst layer and the corresponding growth of the fuel crossover rate as the methanol feed concentration grows [19–21, 24, 56]. The figure also shows the influence of oxygen concentration on fuel utilization. The effect of oxygen concentration is small for low fuel molarities (1 M) due to the low methanol concentrations existing at the anode catalyst layer. By contrast, for larger methanol concentrations the fuel utilization grows with oxygen concentration due to the higher current densities (i.e., methanol conversion rates) achieved as a result of the improved cathode performance, which reduces the amount of unreacted methanol available for crossover at the anode.

An issue that may bring undesirable consequences on DMFC operation is oxygen starvation. As shown before, this scenario is more likely to occur when the methanol crossover flux is high (i.e., at high methanol concentrations) and the oxygen concentration is low. The effect of oxygen starvation on the rib/channel current distribution is examined in Fig. 8. This figure shows the electron current lines, oxygen distribution, and anode and cathode overpotentials at $V_{\text{cell}} = 0.2$ V for a 3 M methanol solution and various oxygen concentrations, $C_{\text{O}_2}^{\text{ch}} = 2, 3.5, \text{ and } 5 \text{ mol/m}^3$ ($\xi_c = 0.7, 1, \text{ and } 1.75$). For illustrative purposes, a 30% compressed GDL is considered. As can be seen, when the oxygen supply is large enough ($C_{\text{O}_2}^{\text{ch}} = 3.5 \text{ and } 5 \text{ mol/m}^3$), the cell operates normally: electrons and protons generated at the anode by the MOR and at the cathode by the parasitic oxidation of methanol are consumed with oxygen at the cathode catalyst layer to produce water, so that the output current is positive in the entire active area. Only an increase of the cathode mixed overpotential under the rib (with the corresponding decrease of the output current) is observed for $C_{\text{O}_2}^{\text{ch}} = 3.5 \text{ mol/m}^3$ due to the limited transport of oxygen towards this region. However, when the availability of oxygen is low ($C_{\text{O}_2}^{\text{ch}} = 2 \text{ mol/m}^3$), strong changes occur in the cell; the high cathode mixed overpotentials ($\eta_c \simeq 0.8 - 0.9$) in the oxygen-starved region under the rib lead to a pronounced decay of the anode overpotential there ($\eta_a \rightarrow 0$). As a result, hydrogen is spontaneously evolved under the anode rib, and the cell operates in a bifunctional regime [79, 84, 108–110]: in the anode the region under the rib consumes the electrons generated under the channel, whereas in the cathode the electrons generated from

the parasitic oxidation of methanol under the rib are consumed under the channel. Accordingly, the flux of protons is directed from cathode to anode under the rib, while it is directed (as usual) from anode to cathode under the channel. This troublesome scenario impacts catalyst durability [92, 94], and leads to a notable reduction of the output current density since a large portion of the electrode consumes current.

4.2. Optimum GDL assembly compression ratio

The next study examines the combined effect of reactant concentrations and GDL assembly compression. Figure 9 shows the variation of the output current density with GDL compression ratio at $V_{\text{cell}} = 0.25$ V for different operating conditions. In the left panel $C_{\text{O}_2}^{\text{ch}}$ is fixed at 3.5 mol/m^3 ($\xi_c = 1$) and $C_{\text{ml}}^{\text{ch}}$ varies between 1, 2, and 3 M, whereas in the right panel $C_{\text{ml}}^{\text{ch}}$ is fixed at 3 M and $C_{\text{O}_2}^{\text{ch}}$ varies between 2, 3.5, and 5 mol/m^3 ($\xi_c = 0.7, 1$, and 1.75). We therefore consider cases in which there are strong mass transport losses at the anode and the cathode, respectively, and these mass transport losses are gradually reduced by increasing the availability of the deficient reactant (see Fig. 7 for details). In addition, two different bipolar plate materials are analyzed: Graphite (G), and stainless steel or Metallic (M), corresponding to low and high GDL/BPP electrical contact resistances, respectively.

As shown in Fig. 9, for a given reactant concentration there is an optimum GDL compression ratio that maximizes the cell performance due to the trade-off between ohmic and concentration losses. For low compression levels the cell performance is degraded by the ohmic losses caused by the inadequate electrical contact at the GDL/BPP interface, whereas excessive compression increases mass transport losses due to the lower porosity and higher tortuosity of mass transport pathways in the GDL [111–114]. The optimal compression strongly depends upon the chosen material, with higher compression levels being required to maximize cell performance with metallic plates owing to the larger electrical contact resistance offered by this type of material [89]. Moreover, it can be seen in Fig. 9 that the optimal compression ratio depends on the actual working conditions. When the cell performance is strongly limited by either methanol or oxygen transport (points A in Fig. 9), a lower compression ratio leads to a better performance due to the dominant effect of concentration losses. However, when the availability of reactants is increased (points B and C in Fig. 9), the optimum compression ratio is shifted to larger values due to the increase of the current densities reached in the cell and, therefore, the larger impact of ohmic losses at the GDL/BPP interface. Note that the absence of performance drop at low compressions for the graphite plates (points A) is due to the exceedingly small ohmic losses exhibited by this material, along with the low current densities typical of DMFCs.

The above results are further illustrated in Fig. 10, which shows the polarization curves corresponding to different GDLs compressed by metallic plates for selected operating conditions chosen from Fig. 9. Figures. 10(a)–(b) examine the effect of methanol concentration. As can be seen, higher compressions are needed to mitigate the adverse effect of electrical contact resistances in Fig. 10(b), in which the current density achieved in the cell is larger as a result of the higher methanol concentration. Similar conclusions can be drawn from Figs. 10(b)–(d), in which oxygen concentration is gradually increased while the methanol concentration is fixed at 3 M. The variations found in the optimum compression

ratio are in qualitative agreement with the experimental studies reported by Zhu et al. [113] and Shrivastava et al. [114] for fully passive and semi-passive liquid-feed DMFCs.

A striking feature that deserves further attention is the high sensitivity of the Open-Circuit Voltage (OCV) with respect to oxygen transport limitations when the cell is operated at high methanol but low oxygen concentrations; a situation illustrated in Fig. 10(c). In this case, an over-compression of the GDL affects the cell performance not only at middle-to-low voltages but also at high voltages due to the high parasitic currents induced by methanol crossover. This causes the polarization curves above the optimum compression ratio to drop as the GDL is compressed and the oxygen supply towards the catalyst layer is reduced. A similar behavior was reported by Zhu et al. [113] when operating their fully and semi-passive cathode feed DMFC with high molarity methanol solutions. Another example of OCV reduction with GDL compression was reported by Shrivastava et al. [114] when increasing the methanol feed concentration in their fully passive DMFC. On the contrary, the impact of GDL compression on the OCV is small when the availability of oxygen at the cathode catalyst layer is not a major issue, as occurs when the cell is operated with low methanol concentrations (i.e., low parasitic currents) and/or high oxygen concentrations; a situation illustrated in Figs. 10(a)–(b)–(d). In this case, GDL compression mainly affects the cell performance at middle-to-low voltages, that is, in the ohmic and concentration regions of the polarization curve [89, 111, 112, 114].

4.3. Effect of the electrical contact resistance between the GDL-MPL diffusion medium and the membrane

The potential effect of the electrical contact resistance between the GDL-MPL diffusion medium and the membrane, $R_c^{\text{gdl/mem}}$, is examined in Fig. 11. The left panel shows the variation of the current density in the regions under the rib and under the channel as a function of the multiplicative factor, $\Pi = 0 - 100$, considered in the correlation for $R_c^{\text{gdl/mem}}$, while the right panel shows the current distribution in the active area for some specific values of Π . The results corresponding to three different cell voltages are presented: $V_{\text{cell}} = 0.4, 0.25, \text{ and } 0.1 \text{ V}$. The methanol and oxygen concentrations are equal to $C_{\text{ml}}^{\text{ch}} = 2 \text{ M}$ and $C_{\text{O}_2}^{\text{ch}} = 3.5 \text{ mol/m}^3$ ($\xi_c = 1$), respectively.

The effect of the contact resistance between the diffusion medium and the membrane grows with the current density, so that it is more relevant at low cell voltages. The performance degradation is mainly concentrated in the region under the channel due to the lower contact pressures transmitted to this region in the cell assembly process [63, 97, 99–102]. As can be seen in Fig. 11(a), at $V_{\text{cell}} = 0.1 \text{ V}$ the current density under the channel drops by a factor of more than 3 when Π is varied from 0 to 100. In contrast, the current density under the rib decreases only by a factor of 2 given the better contact between components in this region. Interestingly, as shown in Fig. 11(b), the current density exhibits a peak under the rib/channel transition region at low cell voltages ($V_{\text{cell}} = 0.1 \text{ V}$) when $\Pi = 20$. As discussed in previous PEMFC studies [102], the existence of a local maximum in the current density distribution is due to the trade-off between the high mass transport losses under the rib and the large ohmic losses under the channel. On the contrary, no peak current densities are observed when the effect of $R_c^{\text{gdl/mem}}$ is neglected or is dramatically increased; e.g., for $\Pi = 0$ the current density peaks under the channel, where mass transport losses are smaller, whereas for $\Pi = 100$ the peak is displaced under the rib due

to the stronger ohmic losses existing under the channel.

4.4. Effect of methanol concentration and cell temperature

In this analysis, the combined effect of fuel molarity and operating temperature on DMFC performance is investigated. Figures 12(a)–(b) show isocontours of the power density and parasitic current density at $V_{\text{cell}} = 0.25 \text{ V}$ as a function of methanol concentration, $C_{\text{ml}}^{\text{ch}}$, and cell temperature, T . In addition, Fig. 12(c) shows the polarization curves corresponding to two methanol concentrations, $C_{\text{ml}}^{\text{ch}} = 2 \text{ M}$ and 5 M , at various specified cell temperatures, $T = 30, 45, 60$, and 80°C . The oxygen concentration is kept equal to $C_{\text{O}_2}^{\text{ch}} = 6 \text{ mol/m}^3$ ($\xi_c = 3.5$) in all cases.

Different effects are triggered when increasing the cell temperature. Many of them are positive: temperature activates reaction kinetics (higher exchange current densities, $i_{0,\text{m}}$ and i_{0,O_2}), reduces the ionic resistivity of the membrane (higher conductivity, $\sigma_{\text{mem}}^{\text{eff}}$), increases the bulk diffusivity of methanol and oxygen (higher bulk diffusivities, $D_{\text{ml,water}}^{\text{bulk}}$, $D_{\text{mv,gas}}^{\text{bulk}}$ and $D_{\text{O}_2,\text{air}}^{\text{bulk}}$), and promotes the phase change rate of liquid methanol to methanol vapor (higher Henry's law constant, $k_{\text{H,m}}$). However, it also has negative consequences: it increases electroosmotic and diffusive transport of methanol/water through the membrane (higher electroosmotic drag coefficients, n_{d}^{m} and n_{d}^{w} , and methanol diffusivity in the membrane, $D_{\text{ml,mem}}^{\text{eff}}$), thereby increasing the methanol-crossover flux and aggravating flooding issues at the cathode [11–15, 17, 21, 22, 51, 56, 72]. In fact, when methanol transport is not a major limitation to cell performance, the enhancement of the mass-transfer rate of liquid methanol with temperature becomes an additional problem due to the increase of methanol crossover.

This complex scenario, typical of liquid-feed DMFCs, is illustrated by Fig. 12. As shown in Figs. 12(a)–(b), due to the trade-off between anode polarization losses and cathode mixed overpotential, the power output is maximized at intermediate methanol concentrations ($C_{\text{ml}}^{\text{ch}} \approx 2 \text{ M}$) and high temperatures ($T \approx 80^\circ\text{C}$). At low-to-intermediate methanol concentrations ($C_{\text{ml}}^{\text{ch}} \lesssim 3 \text{ M}$) the peak power density increases gradually with temperature because the beneficial effects discussed above prevail over the (moderate) detrimental effect of methanol crossover [12, 14, 15, 21, 51, 56]. By contrast, at intermediate-to-high methanol concentrations ($C_{\text{ml}}^{\text{ch}} \gtrsim 3 \text{ M}$) the detrimental effect of crossover takes over and results in an overall reduction of the cell performance. An optimal working temperature arises at $C_{\text{ml}}^{\text{ch}} \gtrsim 3 \text{ M}$: at low-to-intermediate cell temperatures ($T \lesssim 30 - 60^\circ\text{C}$) the performance is enhanced due to the prevalence of the positive effects of temperature; however, the performance is severely degraded when the temperature is too high as a result of the dominant effect of methanol crossover and the associated decay of the cathode performance [14].

The above results are further illustrated in the polarization curves shown in Fig. 12(c). As can be seen, for 1 M methanol the cell operates in the region where the parasitic current remains relatively small, and the power density raises with temperature. On the contrary, for a methanol concentration as high as 5 M the response of the cell lies in the region where an optimum working temperature exists. The cell performance is promoted when the cell temperature is raised from 30°C to 45°C , but decreases from 45°C to 80°C due to the limited availability of oxygen to sustain the high parasitic currents achieved in the cell. It should be noted that the qualitative picture provided by Fig. 12 may

experience some changes for lower oxygen concentrations, so that the detrimental effect of methanol crossover would become dominant both at lower temperatures and lower methanol concentrations.

4.5. Effect of methanol concentration and anode (cathode) gas (liquid) saturation level

Figure 13 shows the influence of methanol concentration, $C_{\text{ml}}^{\text{ch}}$, on power density at $V_{\text{cell}} = 0.25$ V for different anode gas coverage factors, $1 - s_a^{\text{ch}}$, and cathode saturation levels, s_c^{ch} . The oxygen concentration is kept equal to $C_{\text{O}_2}^{\text{ch}} = 6 \text{ mol/m}^3$ ($\xi_c = 3.5$) in all cases.

Examining the effect of the anode gas coverage factor, shown in Fig. 13(a), two regimes can be clearly distinguished. For low methanol concentrations, $C_{\text{ml}}^{\text{ch}} \lesssim 1.8 \text{ M}$, the blockage of liquid methanol transport by gas bubbles is dominant: the reduction of the two-phase mass transport properties of liquid methanol (i.e., liquid-phase relative diffusivity, g_l , and permeability, k_{rl}) with gas saturation reduces the concentration of liquid methanol at the anode catalyst layer, leading to higher anode overpotentials and lower power densities. By contrast, for larger methanol concentrations, $C_{\text{ml}}^{\text{ch}} \gtrsim 1.8 \text{ M}$, gas-phase methanol transport via evaporation/condensation becomes the dominant mass transport mechanism: unlike liquid-phase properties, the transport properties of methanol vapor increase with gas saturation (i.e., gas-phase relative diffusivity, g_g , and permeability, k_{rg}), which promotes methanol condensation and increases the overall mass transport rate of methanol towards the anode catalyst layer. As a result, the cell performance around 2 M methanol improves with gas saturation. This trend is again reversed, however, when methanol concentration becomes so large, $C_{\text{ml}}^{\text{ch}} \gtrsim 3 \text{ M}$, such that the enhanced methanol condensation rate starts to increase methanol crossover, thereby leading to a lower cathode performance.

It is worth noting that the effect of the anode gas coverage factor depends critically on the non-equilibrium phase change formulation ($0 < k_{\text{evp}} \sim k_{\text{con}} < \infty$) adopted in the present work (see Eq. (A.15)) [86]. The scenario discussed above lies between the two extreme cases that result when no phase change ($k_{\text{evp}} = k_{\text{con}} = 0$) or thermodynamic equilibrium conditions ($k_{\text{evp}}, k_{\text{con}} \rightarrow \infty$) are considered. Thus, when $k_{\text{evp}} = k_{\text{con}} = 0$ methanol evaporation/condensation is absent and the transport rate of (liquid) methanol through the GDL always decreases with gas saturation. Consequently, the condensation-dominant region observed in Fig. 13(a) disappears. In contrast, when $k_{\text{evp}}, k_{\text{con}} \rightarrow \infty$, as assumed in other works in the literature [51, 58, 68, 85], the mass-transfer rate of methanol is strongly enhanced with gas saturation due to the large contribution of methanol condensation. Hence, the blockage-dominant region shown in Fig. 13(a) is virtually suppressed. As suggested by Yang & Zhao [71], further research efforts are needed to build up a consensus on the state of methanol vapor in the MEA.

Lastly, we shall focus our attention on the influence of the cathode saturation level. As seen in Fig. 13(b), this parameter has virtually no effect at low methanol concentrations ($C_{\text{ml}}^{\text{ch}} \lesssim 1.5 - 2 \text{ M}$), since methanol transport losses are the dominant mechanism determining cell performance. However, at higher methanol concentrations ($C_{\text{ml}}^{\text{ch}} \gtrsim 1.5 - 2 \text{ M}$), the growth of methanol crossover reverses this situation, making the cell performance very sensitive to the availability of oxygen at the cathode [15, 17, 19, 21, 22, 24, 30, 51, 62]. As a result, the cell performance drops with the cathode

saturation level due to the blockage of oxygen transport towards the cathode catalyst layer. The strong shortage of oxygen at high cathode saturation levels ($s_c^{\text{ch}} = 0.6$, i.e., flooding conditions) precludes the operation of the cell with highly concentrated methanol solutions.

5. Conclusions

A multiphysics 2D/1D across-the channel model has been developed to investigate the combined effects of operating conditions and GDL compression in liquid-feed Direct Methanol Fuel Cells (DMFCs). The model accounts for a 2D description of two-phase transport phenomena at the anode and cathode gas diffusion layers, and relies on a local 1D description to model the electrochemical reactions in the catalyst layers, as well as through-plane mass and charge transport in the microporous layers and the membrane. The predictive capabilities of the model have been successfully validated against previous experimental and numerical results using an extended 3D/1D MEA + 1D channel version to account for the along-the-channel evolution of the different flow variables observed in the experimental setups. Then, a comprehensive parametric study has been carried out on the 2D/1D across-the channel model to examine the impact of key factors affecting cell performance. The variables under study included oxygen and methanol concentrations, GDL compression ratio, bipolar plate material, contact resistance between the GDL-MPL diffusion medium and the membrane, cell temperature, and gas and liquid saturation levels at the anode and cathode GDL/channel interfaces. The following conclusions can be drawn from the study.

There is an optimum methanol concentration ($C_{\text{ml}}^{\text{ch}} \approx 2 \text{ M}$ for the present cell design) that maximizes the power output of liquid-feed DMFCs due to the trade-off between anode polarization losses and the mixed overpotential originated at the cathode by methanol crossover. The detrimental effect due to crossover is aggravated as the availability of oxygen is reduced and the methanol concentration is increased, which gives rise to strong mass transport limitations at the cathode. Oxygen starvation eventually causes the cell to operate in the so-called bifunctional regime; a troublesome operating scenario that may affect catalyst durability.

The fuel utilization decreases with methanol concentration owing to the accumulation of unreacted methanol at the anode catalyst layer and the resulting growth of the methanol crossover rate. For a given cell voltage, the fuel utilization increases with oxygen concentration due to the larger current densities (i.e., methanol consumption rates) achieved in the cell.

There is an optimum GDL compression level that maximizes the cell power output. The optimum largely depends on the electrical contact resistance offered by the GDL/BPP material pair. However, slight variations can also be observed depending on the actual working conditions of the cell, since the optimal compression ratio varies depending on the predominant contribution of ohmic vs. concentration losses. When the availability of oxygen is severely limited (e.g., at high methanol and low oxygen concentrations) assembly compression also affects the cell performance at high cell voltages, leading to a reduction of the open-circuit voltage for increasing GDL compression.

The electrical contact resistance between the diffusion medium and the catalyst-coated membrane degrades the cell performance. The associated ohmic losses are higher in the region under the channel due to the lower contact pressures transmitted to this region during the cell assembly process. At low cell voltages, a local maximum in the current density distribution may arise under the rib/channel transition region due to the trade-off between large electrical contact resistances under the channel and high mass transport limitations under the rib. The precise measurement of this contact resistance have not yet been reported in the open literature, and warrants further work.

At low-to-intermediate methanol concentrations ($C_{ml}^{ch} \lesssim 3 \text{ M}$) the cell performance improves with temperature due to the higher exchange current densities, the lower ionic resistance of the membrane, and the enhanced mass transport rate of reactants. However, an increase of the cell temperature also leads to higher methanol/water crossover fluxes. As a result, the cell performance at intermediate-to-high methanol concentrations ($C_{ml}^{ch} \gtrsim 3 \text{ M}$) exhibits an optimal working temperature: the cell performance improves at moderate temperatures due to the prevalence of the above positive effects, but decreases at elevated temperatures due to the excessive growth of the parasitic current and the corresponding reduction of the cathode performance.

Non-equilibrium phase change of methanol in the anode GDL leads to two opposite effects when the gas coverage factor at the anode GDL/channel interface is increased. At low methanol concentrations, $C_{ml}^{ch} \lesssim 1.8 \text{ M}$, a higher gas saturation level leads to a decrease of the methanol mass-transfer rate through the GDL due to the reduction of the two-phase mass transport properties of liquid methanol (i.e., lower liquid-phase relative diffusivity, g_l , and permeability, k_{rl}). However, a higher gaseous content in the anode GDL also promotes mass transport of methanol vapor (i.e., higher gas-phase relative diffusivity, g_g , and permeability, k_{rg}). As a result, the overall methanol mass-transfer rate is enhanced with gas saturation at high methanol concentrations, $C_{ml}^{ch} \gtrsim 1.8 \text{ M}$, due to the predominant effect of methanol condensation. Additional work is still needed to elucidate the thermodynamic state of methanol vapor in liquid-feed DMFCs. On the other hand, an increase of the cathode liquid saturation level reduces the mass-transfer rate of oxygen towards the cathode catalyst layer. The detrimental effect of flooding is rather small when methanol transport is the limiting mass transport mechanism at low methanol concentrations ($C_{ml}^{ch} \lesssim 1.5 - 2 \text{ M}$), but dramatically reduces the cell performance at elevated methanol concentrations when the parasitic consumption of oxygen is high ($C_{ml}^{ch} \gtrsim 1.5 - 2 \text{ M}$).

The valuable insight gained from the present study motivates further modeling efforts. Future research areas should include the accurate description of two-phase mass transport processes at the GDL/channel interface, the effect of methanol poisoning at the cathode catalyst layer, and the modeling of non-isothermal two-phase flow in the cathode compartment and of the water content in the membrane. In addition, the development of a fully 3D version of the model should be considered to analyze other flow field geometries, such as serpentine or interdigitated channels.

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Appendix A 2D/1D across-the-channel model

The formulation of the 2D/1D across-the-channel model is divided in three parts: the 2D anode and cathode GDL models, and the 1D across-the-membrane model accounting for local through-plane transport processes in both microporous layers and the membrane, in addition to the electrochemical reactions at the catalyst layers. The 1D model assumes that local (macroscopic) transport pathways in these thin layers are straight lines in the through-plane direction. This allows a simplified semi-analytical description of mass and charge transport that results in a significant reduction of computational cost [56, 89]. The mathematical formulation of the 2D anode and cathode GDL models, and of the local 1D model, are presented in this section. Further details on the 2D anode GDL model and the local 1D across-the-membrane model can be found in previous works [56, 86, 89].

The bulk fluid properties, together with the physicochemical and effective transport properties of the anode/cathode GDLs, are summarized in Table 3, whereas the physicochemical and kinetic parameters involved in the 1D model are listed in Table 4. The set of coupled nonlinear governing equations in both GDL sub-models was solved in ANSYS® FLUENT with the segregated solver, using the SIMPLE algorithm to handle the pressure-velocity coupling, a least square cell-based discretization for the gradients, the PRESTO pressure interpolation scheme, and second-order upwind discretization for the momentum, species, and charge conservation equations, the last two implemented through user defined scalars. The convergence criterion for the residuals was set to 10^{-7} , which assured negligible variations in the computed solutions.

In the following, bold symbols denote 2D vectors, e.g., the liquid-phase velocity vector $\mathbf{u}_l = (u_{l,x}, u_{l,y})$, and overlined bold symbols denote second-order tensors, e.g., the absolute or dry permeability tensor

$$\bar{\mathbf{K}} = \begin{bmatrix} K_{xx} & 0 \\ 0 & K_{yy} \end{bmatrix} = \begin{bmatrix} K^{ip} & 0 \\ 0 & K^{tp} \end{bmatrix} \quad (\text{A.1})$$

where the superscripts ip and tp denote the in-plane and through-plane orthotropic tensor components, respectively.

A.1 Anode GDL model

Transport processes in the anode GDL are described by the mass and momentum (i.e., Darcy's law) conservation equations of the gas and liquid phase, (A.2)–(A.5), the species conservation equation of liquid methanol, C_{ml} , methanol vapor, C_{mv} , and water vapor, C_{wv} , (A.6)–(A.8), and the conservation equation of electric charge, (A.9). The mass conservation of the gas phase, (A.4), is written in terms of liquid saturation, s , introducing the relationship between the pressure of the gas and liquid phases given by the capillary pressure, $p_c(s, r_p^{-1}) = p_g - p_l$. The resulting equation takes

into account the variations of capillary pressure due to both local saturation and local porosity (measured by the inverse of the local pore radius, r_p^{-1}) in the GDL [86]. The set of partial differential equations is as follows:

$$\nabla \cdot (\rho_l \mathbf{u}_l) = -M_m \dot{R}_m(x, y) - M_w \dot{R}_w(x, y) \quad (\text{A.2})$$

$$\mathbf{u}_l = -\frac{k_{rl}(x, y)}{\mu_l} \bar{\mathbf{K}}(x, y) \nabla p_l \quad (\text{A.3})$$

$$\nabla \cdot \left[-\frac{\rho_g(x, y) k_{rg}(x, y)}{\mu_g} \bar{\mathbf{K}}(x, y) \left(\frac{\partial p_c}{\partial s} \nabla s + \frac{\partial p_c}{\partial r_p^{-1}} \nabla r_p^{-1} + \nabla p_l \right) \right] = M_m \dot{R}_m(x, y) + M_w \dot{R}_w(x, y) \quad (\text{A.4})$$

$$\mathbf{u}_g = -\frac{k_{rg}(x, y)}{\mu_g} \bar{\mathbf{K}}(x, y) \nabla p_g \quad (\text{A.5})$$

$$\nabla \cdot (\mathbf{u}_l C_{ml}) - \nabla \cdot (\bar{\mathbf{D}}_{ml,l}^{\text{eff}}(x, y) \nabla C_{ml}) = -\dot{R}_m(x, y) \quad (\text{A.6})$$

$$\nabla \cdot (\mathbf{u}_g C_{mv}) - \nabla \cdot \left[\rho_g(x, y) \bar{\mathbf{D}}_{mv,g}^{\text{eff}}(x, y) \nabla \left(\frac{C_{mv}}{\rho_g(x, y)} \right) \right] = \dot{R}_m(x, y) \quad (\text{A.7})$$

$$\nabla \cdot (\mathbf{u}_g C_{wv}) - \nabla \cdot \left[\rho_g(x, y) \bar{\mathbf{D}}_{wv,g}^{\text{eff}}(x, y) \nabla \left(\frac{C_{wv}}{\rho_g(x, y)} \right) \right] = \dot{R}_w(x, y) \quad (\text{A.8})$$

$$\nabla \cdot (-\bar{\sigma}^{\text{eff}}(x, y) \nabla \phi) = 0 \quad (\text{A.9})$$

where $\dot{R}_{m/w}$ denotes the local phase change rate of methanol/water in the GDL, and

$$\bar{\mathbf{D}}_{ij}^{\text{eff}} = \begin{bmatrix} D_{ij}^{\text{eff},ip} & 0 \\ 0 & D_{ij}^{\text{eff},tp} \end{bmatrix} = D_{ij}^{\text{bulk}} \begin{bmatrix} f^{ip}(\varepsilon) g_j^{ip}(s) & 0 \\ 0 & f^{tp}(\varepsilon) g_j^{tp}(s) \end{bmatrix} \quad (\text{A.10})$$

is the effective diffusivity of species i in phase j , being $f^{ip/tp}(\varepsilon) = D_{ij}^{\text{eff,dry},ip/tp} / D_{ij}^{\text{bulk}}$ the normalized dry effective diffusivity, and $g_j^{ip/tp}(s) = D_{ij}^{\text{eff,wet},ip/tp} / D_{ij}^{\text{eff,dry},ip/tp}$ the relative effective diffusivity in phase j ; see nomenclature and Table 3 for details of these and other variables.

According to García-Salaberri et al. [86], the local capillary pressure in the anode GDL is correlated as a function of local pore radius, $r_p(x, y)$, and local saturation, $s(x, y)$, based on the water withdrawal experimental data of Gostick et al. [95]. The capillary pressure curves measured by Gostick et al. [95] for both uncompressed (u) and compressed (c) samples are linearly interpolated by using the inverse of the characteristic pore radius, r_p^{-1} , as representative variable

$$p_c(s, r_p^{-1}) = \beta p_c^u(s) + (1 - \beta) p_c^c(s); \text{ with } \beta = \frac{r_p^{-1} - (r_p^{-1})^c}{(r_p^{-1})^u - (r_p^{-1})^c} \quad (\text{A.11})$$

where the p_c - s curves of the uncompressed and compressed GDL samples are fitted to the following van Genuchten-type equations [95]:

$$p_c(s) = p_g - p_l = p_{c,b} \left[\left(\frac{s - s_r}{1 - s_r} \right)^{-1/n} - 1 \right]^{1/m} - p_{\text{ref}} \quad (\text{A.12})$$

In Eq. (A.11), the local pore radius, $r_p(x, y)$, is computed from the local porosity distribution, $\varepsilon(x, y)$, obtained from the finite element simulations of the GDL assembly process described in Ref. [97], according to [118]:

$$r_p(\varepsilon) = \sqrt{\frac{K_{\text{avg}}(\varepsilon)}{\varepsilon}} \quad (\text{A.13})$$

where $K_{\text{avg}}(\varepsilon) = [K^{\text{ip}}(\varepsilon) + K^{\text{tp}}(\varepsilon)]/2$ is the local average permeability of the GDL. The characteristic mean pore radii of the GDL samples tested by Gostick et al. [95] were estimated from the data reported in their work. The mean pore radius of the uncompressed sample, r_p^u , was calculated using (A.13) with the uncompressed mean porosity, $\varepsilon_{\text{gdl}}^u$, reported by Gostick et al. [95], i.e., $r_p^u = \sqrt{K_{\text{avg}}(\varepsilon_{\text{gdl}}^u)/\varepsilon_{\text{gdl}}^u}$. The mean pore radius of the compressed sample, r_p^c , was determined based on the compressed mean porosity, $\varepsilon_{\text{gdl}}^c$, corresponding to the compression ratio, CR, applied in their experiments [95]:

$$r_p^c = \sqrt{\frac{K_{\text{avg}}(\varepsilon_{\text{gdl}}^c)}{\varepsilon_{\text{gdl}}^c}}; \text{ with } \varepsilon_{\text{gdl}}^c = \frac{\varepsilon_{\text{gdl}}^u - \text{CR}}{1 - \text{CR}} \text{ and } \text{CR} = \frac{\Delta\delta_{\text{gdl}}}{\delta_{\text{gdl}}^u} \quad (\text{A.14})$$

where $\Delta\delta_{\text{gdl}}$ is the decrease of the GDL thickness due to compression, and δ_{gdl}^u and $\varepsilon_{\text{gdl}}^u$ are the uncompressed GDL thickness and mean porosity, respectively.

The phase change rate of methanol ($i = m$) and water ($i = w$) is modeled by the following expression [86]:

$$\dot{R}_i = \begin{cases} k_{\text{evp}} \frac{\varepsilon s X_{il} \rho_l}{M_w} (p_i^{\text{sat}} - p_{iv}) & p_{iv} \leq p_i^{\text{sat}} \\ k_{\text{con}} \frac{\varepsilon (1-s) X_{iv}}{RT} (p_i^{\text{sat}} - p_{iv}) & p_{iv} > p_i^{\text{sat}} \end{cases} \quad (\text{A.15})$$

where X_{il} and X_{iv} are the mole fractions of methanol and water in the liquid and gas phase, respectively, p_{iv} and p_i^{sat} are the partial and saturation pressures of methanol/water vapor, and k_{evp} and k_{con} are the evaporation and condensation rate constants. The saturation pressure of methanol is given by Henry's law as $p_m^{\text{sat}} = k_{H,m}(T) X_{ml}$, while the saturation pressure of water depends only on temperature (see Table 3). The mole fraction of liquid methanol is determined as $X_{ml} = C_{ml}M_l/\rho_l$, so that the mole fraction of liquid water is $X_{wl} = 1 - X_{ml}$. Note that the liquid-phase density and molecular mass are assumed equal to those of water, $\rho_l = \rho_w$ and $M_l = M_w$, given the rather low methanol concentrations typically used in liquid-feed DMFCs. The mole fraction of gaseous species i is calculated according to $X_{iv} = C_{iv}M_g/\rho_g$, where the density of the gas mixture is $\rho_g = C_{mv}M_m + C_{wv}M_w + \left[(p_g/RT) - C_{mv} - C_{wv}\right]M_{\text{CO}_2}$ and the molar mass is $M_g = (Y_{mv}/M_{mv} + Y_{wv}/M_{wv} + Y_{\text{CO}_2}/M_{\text{CO}_2})^{-1}$, with mass fractions Y_i equal to $Y_{mv} = C_{mv}M_m/\rho_g$, $Y_{wv} = C_{wv}M_w/\rho_g$, and $Y_{\text{CO}_2} = \left[(p_g/RT) - C_{mv} - C_{wv}\right]M_{\text{CO}_2}/\rho_g$.

The boundary conditions at the anode GDL/channel interface specify the concentration of liquid methanol, C_{ml}^{ch} , the liquid saturation, s_a^{ch} , and the liquid-phase pressure, $p_{a,l}^{\text{ch}}$, at this interface, where methanol and water vapor are assumed to be in thermodynamic equilibrium, and a no-flux boundary condition is imposed on the electronic potential. At the GDL/BPP interface no-flux conditions are prescribed for all flow and species variables, whereas the electronic potential obeys a mixed boundary condition derived from Ohm's law; this last condition accounts, in particular, for the variation of the GDL/BPP electrical contact resistance, $R_c^{\text{gdl/bpp}}(x)$, with the local interfacial pressure, $p_c^{\text{gdl/bpp}}(x)$ [89]. The local fluxes of water, liquid methanol, and carbon dioxide are conveniently imposed at the GDL/MPL interface; these fluxes result from (i) the electrochemical consumption/production rates plus the crossover of methanol and water ($N_{wl,a}$, N_{ml} , N_{CO_2}), and (ii) the local average phase change rates of methanol/water at the anode microporous layer ($\bar{R}_{m/w,\text{ampl}}$) and

catalyst layer ($\bar{R}_{m/w,ac1}$), which are given by the local 1D model to be presented below. In addition, the local current density, i , generated at the anode catalyst layer is prescribed as boundary condition for the charge conservation equation. The complete set of boundary conditions is summarized below (where $\mathbf{n}$ denotes the outward normal unit vector):

At the GDL/channel interface (thermodynamic equilibrium):

$$\begin{aligned} p_l &= p_{a,l}^{\text{ch}}, \quad s = s_a^{\text{ch}}, \quad C_{ml} = C_{ml}^{\text{ch}}, \\ C_{mv} &= C_{mv}^{\text{ch,sat}}, \quad C_{wv} = C_{wv}^{\text{ch,sat}}, \quad (-\bar{\sigma}^{\text{eff}} \nabla \phi) \cdot \mathbf{n} = 0 \end{aligned} \quad (\text{A.16a})$$

At the GDL/BPP interface:

$$\mathbf{u}_l \cdot \mathbf{n} = 0 \quad (\text{A.17a})$$

$$\left[-\frac{\rho_g(x, y) k_{rg}(x, y)}{\mu_g} \bar{\mathbf{K}}(x, y) \left(\frac{\partial p_c}{\partial s} \nabla s + \frac{\partial p_c}{\partial r_p^{-1}} \nabla r_p^{-1} + \nabla p_l \right) \right] \cdot \mathbf{n} = 0 \quad (\text{A.17b})$$

$$\left(\mathbf{u}_l C_{ml} - \bar{\mathbf{D}}_{ml,l}^{\text{eff}}(x, y) \nabla C_{ml} \right) \cdot \mathbf{n} = 0 \quad (\text{A.17c})$$

$$\left[\mathbf{u}_g C_{mv} - \rho_g(x, y) \bar{\mathbf{D}}_{mv,g}^{\text{eff}}(x, y) \nabla \left(\frac{C_{mv}}{\rho_g(x, y)} \right) \right] \cdot \mathbf{n} = 0 \quad (\text{A.17d})$$

$$\left[\mathbf{u}_g C_{wv} - \rho_g(x, y) \bar{\mathbf{D}}_{wv,g}^{\text{eff}}(x, y) \nabla \left(\frac{C_{wv}}{\rho_g(x, y)} \right) \right] \cdot \mathbf{n} = 0 \quad (\text{A.17e})$$

$$(-\bar{\sigma}^{\text{eff}}(x, y) \nabla \phi) \cdot \mathbf{n} = \frac{\phi}{R_c^{\text{gdl/bpp}}(x)} \quad (\text{A.17f})$$

At the GDL/MPL interface:

$$\begin{aligned} (\rho_l \mathbf{u}_l) \cdot \mathbf{n} = \\ M_w \left(N_{w,l,a}(x) + \bar{R}_{w,ampl}(x) \delta_{\text{ampl}} + \bar{R}_{w,ac1}(x) \delta_{\text{ac1}} \right) + M_m \left(N_{ml}(x) + \bar{R}_{m,ampl}(x) \delta_{\text{ampl}} + \bar{R}_{m,ac1}(x) \delta_{\text{ac1}} \right) \end{aligned} \quad (\text{A.18a})$$

$$\begin{aligned} \left[-\frac{\rho_g(x, y) k_{rg}(x, y)}{\mu_g} \bar{\mathbf{K}}(x, y) \left(\frac{\partial p_c}{\partial s} \nabla s + \frac{\partial p_c}{\partial r_p^{-1}} \nabla r_p^{-1} + \nabla p_l \right) \right] \cdot \mathbf{n} = \\ -M_w \left(\bar{R}_{w,ampl}(x) \delta_{\text{ampl}} + \bar{R}_{w,ac1}(x) \delta_{\text{ac1}} \right) - M_m \left(\bar{R}_{m,ampl}(x) \delta_{\text{ampl}} + \bar{R}_{m,ac1}(x) \delta_{\text{ac1}} \right) - M_{\text{CO}_2} N_{\text{CO}_2}(x) \end{aligned} \quad (\text{A.18b})$$

$$\left(\mathbf{u}_l C_{ml} - \bar{\mathbf{D}}_{ml,l}^{\text{eff}}(x, y) \nabla C_{ml} \right) \cdot \mathbf{n} = N_{ml}(x) + \bar{R}_{m,ampl}(x) \delta_{\text{ampl}} + \bar{R}_{m,ac1}(x) \delta_{\text{ac1}} \quad (\text{A.18c})$$

$$\left[\mathbf{u}_g C_{mv} - \rho_g(x, y) \bar{\mathbf{D}}_{mv,g}^{\text{eff}}(x, y) \nabla \left(\frac{C_{mv}}{\rho_g(x, y)} \right) \right] \cdot \mathbf{n} = -\bar{R}_{m,ampl}(x) \delta_{\text{ampl}} - \bar{R}_{m,ac1}(x) \delta_{\text{ac1}} \quad (\text{A.18d})$$

$$\left[\mathbf{u}_g C_{wv} - \rho_g(x, y) \bar{\mathbf{D}}_{wv,g}^{\text{eff}}(x, y) \nabla \left(\frac{C_{wv}}{\rho_g(x, y)} \right) \right] \cdot \mathbf{n} = -\bar{R}_{w,ampl}(x) \delta_{\text{ampl}} - \bar{R}_{w,ac1}(x) \delta_{\text{ac1}} \quad (\text{A.18e})$$

$$(-\bar{\sigma}^{\text{eff}}(x, y) \nabla \phi) \cdot \mathbf{n} = -i(x) \quad (\text{A.18f})$$

A.2 Cathode GDL model

As in the anode GDL, transport processes in the cathode GDL are modeled by the mass and momentum conservation equations of the gas and liquid phase, (A.19)–(A.21), the species conservation equation of oxygen, (A.22), and the

conservation equation of electric charge, (A.23). Note that, unlike in the anode GDL, the effect of inhomogeneous GDL porosity is neglected in the equation of liquid saturation, (A.21), where the term $(\partial p_c / \partial r_p^{-1}) \nabla r_p^{-1}$ has been dropped as a first approximation. The analysis of the effect of this term in the cathode GDL is out of the scope of this work, although it worths future investigation both in DMFCs and, particularly, in PEMFCs [86, 119–121]. The conservation equation of water vapor is also ignored by considering that the water transported by crossover and generated at the cathode catalyst layer remains in liquid phase (an approach similar to that adopted by others, see, e.g., [62]). The set of governing equations for the cathode GDL is as follows:

$$\nabla \cdot (\rho_g \mathbf{u}_g) = 0 \quad (\text{A.19})$$

$$\mathbf{u}_g = -\frac{k_{rg}(x, y)}{\mu_g} \bar{\mathbf{K}}(x, y) \nabla p_g \quad (\text{A.20})$$

$$\nabla \cdot \left[-\frac{\rho_l k_{rl}(x, y)}{\mu_l} \bar{\mathbf{K}}(x, y) \left(\frac{\partial p_c}{\partial s} \nabla s + \nabla p_g \right) \right] = 0 \quad (\text{A.21})$$

$$\nabla \cdot (\mathbf{u}_g C_{O_2}) - \nabla \cdot (\bar{\mathbf{D}}_{O_2, g}^{\text{eff}}(x, y) \nabla C_{O_2}) = 0 \quad (\text{A.22})$$

$$\nabla \cdot (-\bar{\sigma}^{\text{eff}}(x, y) \nabla \phi) = 0 \quad (\text{A.23})$$

The local capillary pressure in the cathode GDL is expressed as a function of local liquid saturation, $s(x, y)$, and mean porosity, $\varepsilon_{\text{cgdl}}$, based on the semiempirical correlation proposed by Leverett [118]:

$$p_c(s) = p_g - p_l = \sigma \sqrt{\frac{\varepsilon_{\text{cgdl}}}{K_{\text{cgdl, avg}}(\varepsilon_{\text{cgdl}})}} \cos(\theta_{c, \text{cgdl}}) J(s) \quad (\text{A.24})$$

where σ is the surface tension of the immiscible fluid pair, θ_c is the contact angle between both phases, and $J(s)$ is the Leverett J-function,

$$J(s) = \begin{cases} 1.417(1-s) - 2.120(1-s)^2 + 1.263(1-s)^3 & \theta_c \leq 90^\circ \\ 1.417s - 2.120s^2 + 1.263s^3 & \theta_c > 90^\circ \end{cases} \quad (\text{A.25})$$

Although the applicability of this modeling approach, originally proposed for soil porous media, to mixed-wettability GDLs has been debated many times (see [86] and references therein), it is intended to provide a reasonable first approximation to describe capillary transport of water at the cathode (see, e.g., the numerical models in [51, 58, 59, 62, 63] among others). In particular, the use of a common modeling framework for the cathode gas diffusion layer, microporous layer, and catalyst layer enables an easy implementation of the saturation jump condition, given by the continuity of capillary pressure between these three layers (see the formulation of the local 1D model below).

The boundary conditions for the cathode GDL are similar to those of the anode. At the GDL/channel interface, the oxygen concentration, $C_{O_2}^{\text{ch}}$, liquid saturation, s_c^{ch} , and gas-phase pressure, $p_{c, g}^{\text{ch}}$ are prescribed, whereas at the GDL/BPP interface the effect of the (variable) electrical contact resistance, $R_c^{\text{gdl/bpp}}(x)$, on the electronic potential is implemented through a mixed boundary condition. The local mass fluxes at the GDL/MPL interface are given by the molar flux of

oxygen, N_{O_2} , and water, $N_{w,l,c}$, due to the electrochemical reactions and water crossover, whereas the local charge flux is given by the current density, i , consumed at the cathode catalyst layer. The boundary conditions are summarized below:

At the GDL/channel interface:

$$p_g = p_{c,g}^{\text{ch}}, \quad s = s_c^{\text{ch}}, \quad C_{O_2} = C_{O_2}^{\text{ch}}, \quad (-\bar{\sigma}^{\text{eff}} \nabla \phi) \cdot \mathbf{n} = 0 \quad (\text{A.26a})$$

At the GDL/BPP interface:

$$\mathbf{u}_g \cdot \mathbf{n} = 0 \quad (\text{A.27a})$$

$$\left[-\frac{\rho_l k_{rl}(x, y)}{\mu_l} \bar{K}(x, y) \left(\frac{\partial p_c}{\partial s} \nabla s + \nabla p_g \right) \right] \cdot \mathbf{n} = 0 \quad (\text{A.27b})$$

$$(\mathbf{u}_g C_{O_2} - \bar{D}_{O_2,g}^{\text{eff}}(x, y) \nabla C_{O_2}) \cdot \mathbf{n} = 0 \quad (\text{A.27c})$$

$$(-\bar{\sigma}^{\text{eff}}(x, y) \nabla \phi) \cdot \mathbf{n} = -\frac{\phi}{R_c^{\text{gdl/bpp}}(x)} \quad (\text{A.27d})$$

At the GDL/MPL interface:

$$(\rho_g \mathbf{u}_g) \cdot \mathbf{n} = M_{O_2} N_{O_2}(x) \quad (\text{A.28a})$$

$$\left[-\frac{\rho_l k_{rl}(x, y)}{\mu_l} \bar{K}(x, y) \left(\frac{\partial p_c}{\partial s} \nabla s + \nabla p_g \right) \right] \cdot \mathbf{n} = -M_w N_{w,l,c}(x) \quad (\text{A.28b})$$

$$(\mathbf{u}_g C_{O_2} - \bar{D}_{O_2,g}^{\text{eff}}(x, y) \nabla C_{O_2}) \cdot \mathbf{n} = N_{O_2}(x) \quad (\text{A.28c})$$

$$(-\bar{\sigma}^{\text{eff}}(x, y) \nabla \phi) \cdot \mathbf{n} = i(x) \quad (\text{A.28d})$$

A.3 Local 1D across-the-membrane model

The implementation of the local 1D model is divided in two steps [89]. First, the methanol and oxygen concentrations at the catalyst layers, $C_{ml,ac1}(x_i)$ and $C_{O_2,cc1}(x_i)$, and the saturation levels, $s_{ampl}(x_i)$, $s_{cmpl}(x_i)$, $s_{ac1}(x_i)$ and $s_{cc1}(x_i)$, and local average phase change terms, $\bar{R}_{m,ampl}(x_i)$, $\bar{R}_{m,ac1}(x_i)$, $\bar{R}_{w,ampl}(x_i)$ and $\bar{R}_{w,ac1}(x_i)$, at the microporous and catalyst layers, are computed at each computational node x_i from the iterative solution provided by the 2D GDL models at the GDL/MPL interface. Second, the equation for the cell voltage is solved at each computational node x_i , and the output variables provided by the 1D model are passed to the 2D GDL models to update the numerical solution during the convergence process.

Ignoring convective transport, the local methanol concentration at the anode catalyst layer, $C_{ml,ac1}(x_i)$, and the average methanol concentration in the anode microporous layer, $\bar{C}_{ml,ampl}(x_i)$, are given by the following expressions [89]:

$$C_{ml,ac1}(x_i) = C_{ml}^{\text{agdl/ampl}}(x_i) - a \delta_{ampl}^2 - (b - c) \delta_{ampl} \quad (\text{A.29a})$$

$$\bar{C}_{ml,ampl}(x_i) = C_{ml}^{\text{agdl/ampl}}(x_i) - a \frac{\delta_{ampl}^2}{3} - (b - c) \frac{\delta_{ampl}}{2} \quad (\text{A.29b})$$

where $a = \bar{R}_{m,ampl}(x_i)/2D_{ml,ampl}^{eff}(x_i)$, $b = N_{ml}(x_i)/2D_{ml,ampl}^{eff}(x_i)$, and $c = [\bar{R}_{m,ampl}(x_i)\delta_{ampl} - \bar{R}_{m,accl}(x_i)\delta_{accl}]/D_{ml,ampl}^{eff}(x_i)$; $D_{ml,ampl}^{eff}(x_i)$ is the effective diffusivity of liquid methanol in the anode microporous layer, and $\bar{R}_{m,ampl}(x_i)$ and $\bar{R}_{m,accl}(x_i)$ are the local average phase change rates of methanol in the anode microporous layer and catalyst layer, respectively. According to Bruggeman's theory [104], the effective diffusivity is computed as $D_{ml,ampl}^{eff}(x_i) = D_{ml,water}^{bulk} \epsilon_{ampl}^{1.5} s_{ampl}^{1.5}(x_i)$. The phase change rates $\bar{R}_{m,ampl}(x_i)$ and $\bar{R}_{m,accl}(x_i)$ are evaluated using (A.15) with the concentration of methanol vapor at the GDL/MPL interface (directly provided by the 2D anode GDL model), the local saturation level in each layer, and $\bar{C}_{ml,ampl}(x_i)$ and $C_{ml,accl}(x_i)$, respectively. The local saturations at the anode microporous layer, $s_{ampl}(x_i)$, and at the anode catalyst layer, $s_{accl}(x_i)$, are computed as specified ratios of the local saturation at the GDL/MPL interface: $s_{ampl}(x_i)/s_{agdl/ampl}^{agdl/ampl}(x_i) = 0.5$, and $s_{accl}(x_i)/s_{agdl/ampl}^{agdl/ampl}(x_i) = 0.78$ (see Ref. [89] for details). The phase change rates of water, $\bar{R}_{w,ampl}(x_i)$ and $\bar{R}_{w,accl}(x_i)$, are determined like those of methanol using Eq. (A.15).

The local oxygen concentration at the cathode catalyst layer is given by:

$$C_{O_2,ccl}(x_i) = C_{O_2}^{cgdl/cmpl}(x_i) - \left(\frac{\delta_{cmpl}}{D_{O_2,cmpl}^{eff}(x_i)} \right) N_{O_2}(x_i) \quad (A.30)$$

where $D_{O_2,cmpl}^{eff}(x_i) = D_{O_2,air}^{bulk} \epsilon_{cmpl}^{1.5} s_{cmpl}^{1.5}(x_i)$ is the oxygen effective diffusivity in the cathode microporous layer. The local saturation at the cathode microporous layer, $s_{cmpl}(x_i)$, and at the cathode catalyst layer, $s_{ccl}(x_i)$, are obtained from the continuity condition of the capillary pressure at the GDL/MPL and MPL/CL interfaces, $p_c^{cgdl/cmpl}(x_i) = p_{c,cmpl}(x_i) = p_{c,ccl}(x_i)$, that is,

$$\sqrt{\frac{\epsilon_{cgdl}}{K_{cgdl,avg}}} \cos(\theta_{c,cgdl}) J(s_{cgdl/cmpl}^{cgdl/cmpl}(x_i)) = \sqrt{\frac{\epsilon_{cmpl}}{K_{cmpl}}} \cos(\theta_{c,cmpl}) J(s_{cmpl}(x_i)) = \sqrt{\frac{\epsilon_{ccl}}{K_{ccl}}} \cos(\theta_{c,ccl}) J(s_{ccl}(x_i)) \quad (A.31)$$

The nonlinear equations for $s_{cmpl}(x_i)$ and $s_{ccl}(x_i)$ are solved using a standard Newton-Raphson/bisection method [122].

The equations describing mass transport processes in the membrane and the electrochemical reactions at the catalyst layers are presented next. These equations include the balance of electric charge at the catalyst layers, (A.32a); the non-Tafel kinetics of the MOR at the anode catalyst layer, (A.32b); the inverse Tafel kinetics of the HER at the anode catalyst layer (A.32c); the first-order Tafel kinetics of the ORR at the cathode catalyst layer, (A.32d); the parasitic current due to complete methanol oxidation at the cathode catalyst layer, (A.32e); the methanol-crossover flux across the membrane (by diffusion and electroosmotic drag), (A.32f); and the fluxes of methanol, oxygen, water, and carbon dioxide at the anode/cathode catalyst layers, including the effect of electroosmotic transport of water, (A.32g)–(A.32k). The resulting algebraic system of equations, to be solved for each computational node x_i in the in-plane direction, is as follows:

$$i(x_i) = i_{MOR}(x_i) - i_{HER}(x_i) = i_{ORR}(x_i) - i_p(x_i) \quad (A.32a)$$

$$i_{MOR}(x_i) = \delta_{accl} a_a i_{0,m} \frac{\kappa C_{ml,accl}(x_i) \exp\left(\frac{\alpha_m F}{RT} \eta_a(x_i)\right)}{C_{ml,accl}(x_i) + \lambda \exp\left(\frac{\alpha_m F}{RT} \eta_a(x_i)\right)} \quad (A.32b)$$

$$i_{HER}(x_i) = \delta_{accl} i_{0,H_2} \exp\left\{-\frac{\alpha_{H_2} F}{RT} \left[\left(U_{MOR}^0 - U_{HER}^0 \right) + \eta_a(x_i) \right] \right\} \quad (A.32c)$$

$$i_{\text{ORR}}(x_i) = (1 - s_{\text{ccl}}(x_i)) \delta_{\text{ccl}} a_c i_{0,\text{O}_2} \left(\frac{C_{\text{O}_2,\text{ccl}}(x_i)}{k_{\text{H},\text{O}_2} C_{\text{O}_2,\text{ref}}} \right) \exp \left(\frac{\alpha_{\text{O}_2} F}{RT} \eta_c(x_i) \right) \quad (\text{A.32d})$$

$$i_p(x_i) = 6F N_{\text{ml,cross}}(x_i) \quad (\text{A.32e})$$

$$N_{\text{ml,cross}}(x_i) = n_d^{\text{m}}(x_i) \frac{i(x_i)}{F} + \frac{D_{\text{ml,mem}}^{\text{eff}}}{\delta_{\text{mem}}} C_{\text{ml,acl}}(x_i); \quad n_d^{\text{m}}(x_i) = \frac{M_w}{\rho_w} n_d^{\text{w}} C_{\text{ml,acl}}(x_i) \quad (\text{A.32f})$$

$$N_{\text{ml}}(x_i) = \frac{i_{\text{MOR}}(x_i)}{6F} + N_{\text{ml,cross}}(x_i) \quad (\text{A.32g})$$

$$N_{\text{O}_2}(x_i) = \frac{i_{\text{ORR}}(x_i)}{4F} = \frac{i(x_i) + i_p(x_i)}{4F} \quad (\text{A.32h})$$

$$N_{\text{wl,a}}(x_i) = \frac{i(x_i)}{6F} + N_{\text{wl,cross}}(x_i); \quad N_{\text{wl,cross}}(x_i) = n_d^{\text{w}} \frac{i(x_i)}{6F} \quad (\text{A.32i})$$

$$N_{\text{wl,c}}(x_i) = \frac{3i_{\text{ORR}}(x_i) - i_p(x_i)}{6F} + N_{\text{wl,cross}}(x_i) = \frac{3i(x_i) + 2i_p(x_i)}{6F} + N_{\text{wl,cross}}(x_i) \quad (\text{A.32j})$$

$$N_{\text{CO}_2}(x_i) = \frac{i_{\text{MOR}}(x_i)}{6F} \quad (\text{A.32k})$$

where the term $1 - s_{\text{ccl}}(x_i)$ in Eq. (A.32d) takes into account the reduction of the active area available for reaction at the cathode catalyst layer due to the blockage of liquid water. For further details on the HER kinetics the reader is referred to Refs. [79, 84], while further information on the remaining kinetic and transport equations can be found elsewhere (see, e.g., [56, 62, 86, 89]).

The algebraic solution of the system of Eqs. (A.32a)–(A.32f) provides expressions for the anode and cathode overpotentials, $\eta_a(x_i)$ and $\eta_c(x_i)$, as a function of the current density, $i(x_i)$, and the methanol and oxygen concentrations at the catalyst layers, $C_{\text{ml,acl}}(x_i)$ and $C_{\text{O}_2,\text{ccl}}(x_i)$. The resulting expressions are then introduced in the equation for the cell voltage, V_{cell} , to obtain the following nonlinear relation among $i(x_i)$, $C_{\text{ml,acl}}(x_i)$, $C_{\text{O}_2,\text{ccl}}(x_i)$, $\phi^{\text{agdl/ampl}}(x_i)$, $\phi^{\text{cgdl/cmpl}}(x_i)$, and V_{cell} :

$$f(i, C_{\text{ml,acl}}, C_{\text{O}_2,\text{ccl}}, \phi^{\text{agdl/ampl}}, \phi^{\text{cgdl/cmpl}}, V_{\text{cell}}) \equiv E_{\text{cell}} - V_{\text{cell}} - \eta_a - \eta_c - \left(\frac{\delta_{\text{mem}}}{\sigma_{\text{mem}}^{\text{eff}}} + 2R_c^{\text{gdl/mem}} \right) |i| - \phi^{\text{agdl/ampl}} + \phi^{\text{cgdl/cmpl}} = 0 \quad \forall x_i \quad (\text{A.33})$$

where E_{cell} is the ideal thermodynamic cell voltage, and the terms $(\delta_{\text{mem}}/\sigma_{\text{mem}}^{\text{eff}})|i(x_i)|$, $2R_c^{\text{gdl/mem}}(x_i)|i(x_i)|$, $\phi^{\text{agdl/ampl}}(x_i)$, and $\phi^{\text{cgdl/cmpl}}(x_i)$ represent the local voltage drop across the membrane, at the anode and cathode interfaces between the GDL-MPL diffusion medium and the membrane, and through the anode and cathode GDLs, respectively. Ohmic losses in the microporous and catalyst layers are neglected since they are typically much smaller than those of the thick membranes used in DMFCs [86, 89]. The absolute value in the current density accounts for the possibility of negative currents.

For a given cell voltage, V_{cell} , the solution of Eq. (A.33) using a Newton-Raphson/Bisection method [122] determines the local current density $i(x_i)$ at each computational node x_i of the anode and cathode catalyst layers during the iterative process. The computed distribution of local current density, and the associated mass transport fluxes at the catalyst layers, Eqs. (A.32g)–(A.32k), couple the anode and cathode 2D GDL models through the local 1D model by means of boundary

conditions (A.18a)–(A.18f) and (A.28a)–(A.28d), thereby closing the mathematical problem.

The average value of the different variables of interest ($\Omega = I, I_p$, etc.) is determined during a postprocessing step by averaging their associated distributions ($\omega(x) = i(x), i_p(x)$, etc.) over the cell active area, A_{cl} :

$$\Omega = \frac{1}{A_{cl}} \int_{A_{cl}} \omega dA \quad (A.34)$$

Appendix B 1D model for anode and cathode channels

Multiphase mass transport in the anode and cathode channels is modeled according to the 1D formulation presented by Wang & Wang [51], Yang et al. [59], and Yang & Zhao [70]. A drift-flux model is used to describe the bubbly-slug flow typically found in the anode stream of liquid-feed DMFCs, while a homogeneous mist-flow model is adopted for the cathode channel. The system of ordinary differential equations resulting from both models is solved numerically using a fourth-order Runge-Kutta scheme [122], considering a spatial step equal to $\Delta z_{ch} = L_{ch}/(N_{stations} - 1)$ between the interior stations, and $\Delta z_{ch}/2$ from the inlet to the first station and from the last station to the outlet. The interfacial fluxes at the GDL/channel interface are linearly interpolated for the evaluation of the derivatives at the midpoint between integration points in the Runge-Kutta method. Note that the total number of integration points used in the simulations is $N_{stations} + 2$ (i.e., $N_{stations}$ interior nodes + 2 inlet/outlet nodes).

The mass, momentum, and species conservation equations governing the evolution of the cross-sectional averaged liquid- and gas-phase velocities, $\bar{u}_{a,l}^{ch}$ and $\bar{u}_{a,g}^{ch}$, liquid saturation, $\bar{s}_a^{ch}$, liquid-phase pressure, $\bar{p}_{a,l}^{ch}$, and liquid methanol concentration, $\bar{C}_{ml}^{ch}$, along the anode flow channel (z -coordinate) are as follows:

$$A_{ch} \frac{d(\rho_l \bar{s}_a^{ch} \bar{u}_{a,l}^{ch})}{dz} = 2w_{ch} \dot{m}_l^{agdl/ch} \quad (B.1)$$

$$A_{ch} \frac{d(\rho_g (1 - \bar{s}_a^{ch}) \bar{u}_{a,g}^{ch})}{dz} = 2w_{ch} \dot{m}_g^{agdl/ch} \quad (B.2)$$

$$\frac{1}{2} \frac{d(\rho_l \bar{s}_a^{ch} \bar{u}_{a,l}^{ch} \bar{u}_{a,l}^{ch})}{dz} = -\frac{d\bar{p}_{a,l}^{ch}}{dz} - \frac{1}{2} (\rho_l \bar{s}_a^{ch}) \frac{f_{mp}}{d_h} (\bar{u}_{a,l}^{ch})^2 \quad (B.3)$$

$$A_{ch} \frac{d(\bar{s}_a^{ch} \bar{u}_{a,l}^{ch} \bar{C}_{ml}^{ch})}{dz} = 2w_{ch} N_{ml}^{agdl/ch} \quad (B.4)$$

where $\dot{m}_l^{agdl/ch}$, $\dot{m}_g^{agdl/ch}$ and $N_{ml}^{agdl/ch}$ are the interfacial liquid-/gas-phase mass fluxes and the molar flux of liquid methanol at the anode GDL/channel interface, f_{mp} is the multiphase friction factor, $A_{ch} = H_{ch} 2w_{ch} - A_{ch,gdl}$ is the effective cross-sectional area of the flow channel, equal to the area of the rectangular channel minus the portion of intruded GDL due to assembly compression, and $d_h = 4A_{ch}/P_{ch}$ is the hydraulic diameter of the channel, being P_{ch} the effective perimeter of the channel. The multiphase friction factor is calculated from the expression for a fully-developed laminar flow, $f_{mp} = 64/Re_{mp}$ [115], where the Reynolds number, $Re_{mp} = \dot{m}_{mp} d_h / \mu_{mp}$, is determined using the local mass flow rate, $\dot{m}_{mp} = \bar{s}_a^{ch} \rho_l \bar{u}_{a,l}^{ch} + (1 - \bar{s}_a^{ch}) \rho_g \bar{u}_{a,g}^{ch}$, and the local volume-weighted dynamic viscosity, $\mu_{mp} = \bar{s}_a^{ch} \mu_l + (1 - \bar{s}_a^{ch}) \mu_g$, of

the fluid stream; ρ_g is assumed equal to 1.145 kg/m^3 . Note that $\dot{m}_l^{\text{agdl/ch}}$, $\dot{m}_g^{\text{agdl/ch}}$ and $N_m^{\text{agdl/ch}}$ are the double of those computed by the 3D/1D model since only the region comprised between the mid-plane of a channel and that of the neighboring rib is included in the numerical domain (see Fig. 2).

According to the drift-flux model, the gas- and liquid-phase velocities are related by:

$$\bar{u}_{a,g}^{\text{ch}} = \frac{C_0 \bar{s}_a^{\text{ch}} \bar{u}_{a,l}^{\text{ch}} + u_{\text{gj}}}{1 - C_0 (1 - \bar{s}_a^{\text{ch}})} \quad (\text{B.5})$$

where the distribution factor, C_0 , and the liquid/gas buoyancy-induced slip velocity, u_{gj} , corresponding to bubbly-slug flow in a rectangular channel are given by:

$$C_0 = \left(1.35 - 0.35 \sqrt{\frac{\rho_g}{\rho_l}} \right) \left[1 - \exp \left(-18 (1 - \bar{s}^{\text{ch}}) \right) \right] \quad (\text{B.6})$$

$$u_{\text{gj}} = \left(0.23 + 0.13 \frac{H_{\text{ch}}}{2w_{\text{ch}}} \right) \sqrt{\frac{(\rho_l - \rho_g) 2w_{\text{ch}} \mathbf{g} \cdot \mathbf{n}_{\text{ch}}}{\rho_l}} \quad (\text{B.7})$$

where $\mathbf{g}$ is the gravity vector, and $\mathbf{n}_{\text{ch}}$ is the normal unit vector in the along-the-channel z -direction.

Similarly, the conservation equations in the cathode channel take the form:

$$A_{\text{ch}} \frac{d(\rho_l \bar{s}_c^{\text{ch}} \bar{u}_{c,l}^{\text{ch}})}{dz} = 2w_{\text{ch}} \dot{m}_l^{\text{cgdl/ch}} \quad (\text{B.8})$$

$$A_{\text{ch}} \frac{d(\rho_g (1 - \bar{s}_c^{\text{ch}}) \bar{u}_{c,g}^{\text{ch}})}{dz} = 2w_{\text{ch}} \dot{m}_g^{\text{cgdl/ch}} \quad (\text{B.9})$$

$$\frac{1}{2} \frac{d(\rho_g (1 - \bar{s}_c^{\text{ch}}) \bar{u}_{c,g}^{\text{ch}} \bar{u}_{c,g}^{\text{ch}})}{dz} = -\frac{d\bar{p}_{c,g}^{\text{ch}}}{dz} - \frac{1}{2} [\rho_g (1 - \bar{s}_c^{\text{ch}})] \frac{f_{\text{mp}}}{d_h} (\bar{u}_{c,g}^{\text{ch}})^2 \quad (\text{B.10})$$

$$A_{\text{ch}} \frac{d((1 - \bar{s}_c^{\text{ch}}) \bar{u}_{c,g}^{\text{ch}} \bar{C}_{\text{O}_2}^{\text{ch}})}{dz} = 2w_{\text{ch}} N_{\text{O}_2}^{\text{cgdl/ch}} \quad (\text{B.11})$$

where $\dot{m}_l^{\text{cgdl/ch}}$, $\dot{m}_g^{\text{cgdl/ch}}$, and $N_{\text{O}_2}^{\text{cgdl/ch}}$ are the interfacial liquid-/gas-phase mass fluxes and the molar flux of oxygen at the cathode GDL/channel interface, respectively. The expression for the multiphase friction factor, f_{mp} , is similar to that of the anode side. In addition, it is assumed that two-phase flow in the cathode channel is homogenous, i.e., $\bar{u}_{c,l}^{\text{ch}} = \bar{u}_{c,g}^{\text{ch}}$. The exchange fluxes, $\dot{m}_l^{\text{cgdl/ch}}$, $\dot{m}_g^{\text{cgdl/ch}}$ and $N_{\text{O}_2}^{\text{cgdl/ch}}$, are also the double of those computed by the 3D/1D model due to the symmetry of the MEA domain used in the simulations.

The flow properties at the channel inlets are determined from the reactant feed conditions. Thus, the methanol and oxygen feed concentrations, $\bar{C}_{\text{ml}}^{\text{ch}}$ and $\bar{C}_{\text{O}_2}^{\text{ch}}$, inlet anode and cathode saturation levels, $\bar{s}_a^{\text{ch}}$ and $\bar{s}_c^{\text{ch}}$, anode liquid-phase velocity, $\bar{u}_{a,l}^{\text{ch}}$, cathode gas-phase velocity, $\bar{u}_{c,g}^{\text{ch}}$, anode liquid-phase pressure, $\bar{p}_{a,l}^{\text{ch}}$, and cathode gas-phase pressure, $\bar{p}_{c,g}^{\text{ch}}$, are specified at $z = 0$:

$$\bar{C}_{\text{ml}}^{\text{ch}}(0) = \bar{C}_{\text{ml}}^{\text{ch,in}}, \bar{C}_{\text{O}_2}^{\text{ch}}(0) = \bar{C}_{\text{O}_2}^{\text{ch,in}}, \bar{s}_a^{\text{ch}}(0) = 1; \bar{s}_c^{\text{ch}}(0) = 0 \quad (\text{B.12})$$

$$\bar{u}_{a,l}^{\text{ch}}(0) = \bar{u}_{a,l}^{\text{ch,in}}, \bar{u}_{c,g}^{\text{ch}}(0) = \bar{u}_{c,g}^{\text{ch,in}}, \bar{p}_{a,l}^{\text{ch}}(0) = \bar{p}_{a,l}^{\text{ch,in}}, \bar{p}_{c,g}^{\text{ch}}(0) = \bar{p}_{c,g}^{\text{ch,in}} \quad (\text{B.13})$$

The saturation level and pressure at the GDL/channel interface are assumed to be equal to their cross-sectional averaged values in the channel, whereas the methanol and oxygen concentrations are assumed to suffer a non-negligible drop between the bulk channel and the GDL/channel interface due to mass transport resistance, i.e.,

$$s_a^{\text{ch}} = \bar{s}_a^{\text{ch}}, s_c^{\text{ch}} = \bar{s}_c^{\text{ch}}, p_{a,l}^{\text{ch}} = \bar{p}_{a,l}^{\text{ch}}, p_{c,g}^{\text{ch}} = \bar{p}_{c,g}^{\text{ch}} \quad (\text{B.14})$$

$$C_{\text{ml}}^{\text{ch}} = \bar{C}_{\text{ml}}^{\text{ch}} + N_{\text{ml}}^{\text{agdl/ch}} / h^{\text{agdl/ch}}, C_{\text{O}_2}^{\text{ch}} = \bar{C}_{\text{O}_2}^{\text{ch}} + N_{\text{O}_2}^{\text{cgdl/ch}} / h^{\text{cgdl/ch}} \quad (\text{B.15})$$

Note that the continuity condition prescribed for the saturation and pressure is equal to that considered in several numerical studies [59, 60, 70], although it differs from that considered in other modeling attempts [51]. Further efforts should be devoted in the future to the modeling of the entrance conditions at the GDL/channel interface.

The anode and cathode mass-transfer coefficients, $h^{\text{agdl/ch}}$ and $h^{\text{cgdl/ch}}$, are estimated as:

$$h^{\text{agdl/ch}} = \text{Sh}_a \frac{D_{\text{ml,ch}}^{\text{eff}}}{d_h}; h^{\text{cgdl/ch}} = \text{Sh}_c \frac{D_{\text{O}_2,\text{ch}}^{\text{eff}}}{d_h} \quad (\text{B.16})$$

where Sh_a and Sh_c are the anode and cathode Sherwood numbers, and $D_{\text{ml,ch}}^{\text{eff}}$ and $D_{\text{O}_2,\text{ch}}^{\text{eff}}$ are the effective diffusivities of methanol and oxygen at the GDL/channel interface, respectively. As a first approximation, the Sherwood numbers are assumed to be those given by Koz & Kandlikar [96] for fully-developed laminar flow, $\text{Sh}_a = \text{Sh}_c = 3.36$, whereas the effective diffusivities, $D_{\text{ml,ch}}^{\text{eff}}$ and $D_{\text{O}_2,\text{ch}}^{\text{eff}}$, are taken linearly proportional to the volume capacity of the transported species, i.e., $D_{\text{ml,ch}}^{\text{eff}} = D_{\text{ml}} s_a^{\text{ch}}$ and $D_{\text{O}_2,\text{ch}}^{\text{eff}} = D_{\text{O}_2} (1 - s_c^{\text{ch}})$.

List of Symbols

A	cross-sectional area [m^2]
a	catalyst surface area per unit volume [m^{-1}]
C	molar concentration [mol m^{-3}]
$\bar{C}^{\text{ch}}$	cross-sectional averaged concentration in the channel; see Appendix B [mol m^{-3}]
C_0	distribution factor; see Eq. (B.6)
$\bar{\mathbf{D}}$	mass diffusivity tensor [$\text{m}^2 \text{s}^{-1}$]
$\bar{\mathbf{D}}_c$	capillary diffusivity tensor [$\text{kg m}^{-1} \text{s}^{-1}$]
E_{cell}	ideal thermodynamic cell voltage [V]
d_h	hydraulic diameter [m]
F	Faraday's constant [C mol^{-1}]
f	friction factor
$f(\varepsilon)$	normalized dry effective diffusivity
$g_j(s)$	relative effective diffusivity in phase j
H	height [m]

h	mass-transfer coefficient; see Eq. (B.16) [m/s]
I	average current density [A m^{-2}]
I_{lim}	limiting current density [A m^{-2}]
I_p	average parasitic current density [A m^{-2}]
i	local current density [A m^{-2}]
i_p	local parasitic current density [A m^{-2}]
i_0	exchange current density [A m^{-2}]
$J(s)$	Leverett J-function; see Eq. (A.25)
$\bar{K}$	absolute permeability tensor [m^2]
k_H	Henry's law constant (methanol [Pa], oxygen [-])
k_{evp}	evaporation rate constant [Pa s^{-1}]
k_{con}	condensation rate constant [s^{-1}]
k_r	relative permeability
L	channel length [m]
M	molecular weight or mole mass [kg mol^{-1}]
m	van Genuchten constant; see Eq. (A.12)
$\dot{m}$	mass flux [$\text{kg m}^{-2} \text{s}^{-1}$]
N	molar flux [$\text{mol m}^{-2} \text{s}^{-1}$]
N_{stations}	number of stations in the 3D/1D MEA + 1D channel model
n	van Genuchten constant; see Eq. (A.12)
$\mathbf{n}$	outward normal unit vector
n_d^i	electroosmotic drag coefficient of species i
P	power density [W m^{-2}]; perimeter [m]
p	static pressure [Pa]
$\bar{p}^{\text{ch}}$	cross-sectional averaged pressure in the channel; see Appendix B [Pa]
p_c	capillary pressure, defined as $p_c = p_g - p_l$ [Pa]
$p_{c,b}$	van Genuchten constant; see Eq. (A.12) [Pa]
$p_c^{\text{gdl/bpp}}$	contact pressure at the GDL/BPP interface [Pa]
$p_c^{\text{gdl/mem}}$	contact pressure between the GDL-MPL diffusion medium and the membrane [Pa]
R	universal gas constant [$\text{J mol}^{-1} \text{K}^{-1}$]
R_c	electrical contact resistance [Ωm^2]
Re	Reynolds number
$\dot{R}$	interfacial mass-transfer rate [$\text{mol m}^{-3} \text{s}^{-1}$]

r	fillet radius [m]
r_p	characteristic pore radius; see Eq. (A.13) [m]
Sh	Sherwood number; see Eq. (B.16)
s	liquid saturation
$\bar{s}^{\text{ch}}$	cross-sectional averaged saturation in the channel; see Appendix B
s_r	residual liquid saturation; see Eq. (A.12)
T	cell temperature [K]
$\mathbf{u}$	(superficial) velocity vector [m s^{-1}]
$\bar{\mathbf{u}}^{\text{ch}}$	cross-sectional averaged velocity in the channel; see Appendix B [m/s]
u_{gj}	buoyancy-induced slip velocity; see Eq. (B.7) [m s^{-1}]
V	voltage [V]
w	half-width [m]
X_i	mole fraction of species i
x	in-plane coordinate [m]
x_i	local in-plane coordinate in the 1D model [m]
Y_i	mass fraction of species i
y	through-plane coordinate [m]
z	longitudinal coordinate along the channel [m]

Greek symbols

α	transfer coefficient
β	interpolation parameter; see Eq. (A.11)
Δ	increment
δ	thickness [m]
ε	(dry) porosity
η	overpotential [V]
θ_c	contact angle [°]
κ	MOR kinetic parameter
λ	MOR kinetic parameter [mol m^{-3}]
μ	dynamic viscosity [$\text{kg m}^{-1} \text{s}^{-1}$]
ξ	stoichiometric ratio
Π	multiplicative factor associated to $R_c^{\text{gdl/mem}}$
ρ	density [kg m^{-3}]

σ	interfacial tension [N m^{-1}]; proton and electrical conductivity [S m^{-1}]
$\bar{\sigma}$	electrical conductivity tensor [S m^{-1}]
ϕ	electronic potential [V]
Ω	mute variable; see Eq. (A.34)
ω	mute variable; see Eq. (A.34)

Subscripts

a	anode
acl	anode catalyst layer
agdl	anode GDL
ampl	anode MPL
avg	average value
c	cathode
cl	catalyst layer
ccl	cathode catalyst layer
cgdl	cathode GDL
cmpl	cathode MPL
ch	channel
cross	crossover
g	gas phase
gdl	gas diffusion layer
i	species i
j	phase j (= l/g, or liquid/gas phase)
l	liquid phase
m	methanol
mp	multiphase conditions
mem	membrane
ml	liquid methanol
mv	methanol vapor
ref	reference value
rib	bipolar plate rib
w	water
wl	liquid water

wv water vapor

Superscripts

agdl/ch	anode GDL/channel interface
agdl/ampl	anode GDL/MPL interface
bulk	bulk property
c	compressed
cgdl/ch	cathode GDL/channel interface
ch	inlet condition at the GDL/channel interface
dry	dry conditions
eff	effective
gdl/bpp	gas diffusion layer/bipolar plate interface
gdl/mem	GDL-MPL diffusion medium/PEM interface
in	inlet feed condition of the channel stream
ip	in-plane direction
out	outlet condition of the channel stream
sat	saturated conditions
T	total
tp	through-plane direction
u	uncompressed
wet	multiphase flow conditions

Abbreviations & Acronyms

1D	one-dimensional
2D	two-dimensional
3D	three-dimensional
BPP	bipolar plate
CL	catalyst layer
CR	compression ratio, defined as $CR = (\delta_{gdl}^u - \delta_{gdl}^c) / \delta_{gdl}^u$
DMFC	direct methanol fuel cell
FU	fuel utilization, defined as $FU = I / (I + I_p)$
GDL	gas diffusion layer
HER	hydrogen evolution reaction

M ²	multiphase mixture
MEA	membrane electrode assembly
MOR	methanol oxidation reaction
MPL	microporous layer
ORR	oxygen reduction reaction
OCV	open-circuit voltage
PEM	proton exchange membrane
PEMFC	proton exchange membrane fuel cell

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Tables

Table 1: Geometrical parameters and uncompressed GDL porosity.

Parameter	Symbol	Value
Rib half-width	w_{rib}	0.5 mm
Rib fillet radius	r_{rib}	40 μm
Distance rib/channel mid-planes	w_{gdl}	1 mm
Uncompressed GDL thickness	$\delta_{\text{agdl}}^u, \delta_{\text{cgdl}}^u$	280 μm (Toray [®] TGP-H-090) [98]
Uncompressed GDL porosity	$\varepsilon_{\text{agdl}}^u, \varepsilon_{\text{cgdl}}^u$	0.78 (Toray [®] TGP-H-090) [98]
Membrane thickness	δ_{mem}	125 μm (Nafion [®] 115) [3]
MPL thickness	$\delta_{\text{ampl}}, \delta_{\text{cmpl}}$	20 μm [35]
CL thickness	$\delta_{\text{acl}}, \delta_{\text{ccl}}$	30 μm [55]

Table 2: Breakdown of cases under study; the ranges of the variables examined in each case are shown underlined.

Variables Under Study	Range							
	$C_{\text{ml}}^{\text{ch}}$ [M]	$C_{\text{O}_2}^{\text{ch}}$ [mol/m ³]	CR [%]	$R_{\text{c}}^{\text{gdl/bpp}}$	Π^1	T [°C]	$1 - s_{\text{a}}^{\text{ch}}$	s_{c}^{ch}
$C_{\text{ml}}^{\text{ch}}, C_{\text{O}_2}^{\text{ch}}$	<u>1, 2, 3</u>	<u>2–5</u>	10	G	0	70	0.3	0.4
$C_{\text{ml}}^{\text{ch}}, C_{\text{O}_2}^{\text{ch}}, \text{CR}, R_{\text{c}}^{\text{gdl/bpp}}$	<u>1, 2, 3</u>	<u>2, 3.5, 5</u>	<u>1–50</u>	<u>G/M²</u>	0	70	0.3	0.4
$R_{\text{c}}^{\text{gdl/mem}}$	2	3.5	10	G	<u>0–100</u>	70	0.3	0.4
$C_{\text{ml}}^{\text{ch}}, T$	<u>0.1–6</u>	6	10	G	0	<u>30–80</u>	0.3	0.4
$C_{\text{ml}}^{\text{ch}}, 1 - s_{\text{a}}^{\text{ch}}, s_{\text{c}}^{\text{ch}}$	<u>0.1–4</u>	6	10	G	0	70	<u>0.1, 0.3, 0.6</u>	<u>0.2, 0.4, 0.6</u>

¹ Π is a variable multiplicative factor applied on the contact resistance $R_{\text{c}}^{\text{gdl/mem}}$ between the GDL-MPL diffusion medium and the membrane.

² G stands for graphite and M for metallic (i.e., stainless steel) BPPs.

Table 3: Bulk fluid properties and physicochemical and effective transport properties of the anode and cathode GDLs (agdl/cgdl).

Parameter	Symbol	Value	Reference(s)
Density of anode liquid mixture (water)	ρ_l	$1000 - 0.0178 (T - 277.15)^{1.7} \text{ kg m}^{-3}$	[115]
Dynamic viscosity of anode liquid mixture (water)	μ_l	$0.458509 - 5.30474 \times 10^{-3} T + 2.31231 \times 10^{-5} T^2 - 4.49161 \times 10^{-8} T^3 + 3.27681 \times 10^{-11} T^4 \text{ kg m}^{-1} \text{ s}^{-1}$	[115]
Density of gas mixture (agdl/cgdl)	ρ_g	Computed/ 1.145 kg m^{-3}	[71]
Dynamic viscosity of anode and cathode gas mixture	μ_g	$2.03 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$	[71]
Bulk diffusivity of liquid methanol	$D_{\text{ml,water}}^{\text{bulk}}$	$10^{-5.4163 - (999.787/T)} \text{ m}^2 \text{ s}^{-1}$	[116]
Bulk diffusivity of methanol vapor	$D_{\text{mv,gas}}^{\text{bulk}}$	$-6.954 \times 10^{-6} + 4.5986 \times 10^{-8} T + 9.4979 \times 10^{-11} T^2 \text{ m}^2 \text{ s}^{-1}$	[71]
Bulk diffusivity of water vapor	$D_{\text{wv,gas}}^{\text{bulk}}$	$2.56 \times 10^{-5} \left(\frac{T}{307.15} \right)^{2.334} \text{ m}^2 \text{ s}^{-1}$	[71]
Bulk diffusivity of oxygen	$D_{\text{O}_2,\text{air}}^{\text{bulk}}$	$2.5 \times 10^{-5} \left(\frac{T}{298} \right)^{3/2} \left(\frac{1.013 \times 10^5}{p_c^{\text{ch}}} \right) \text{ m}^2 \text{ s}^{-1}$	[117]
Evaporation rate constant of methanol and water	k_{evp}	$10^{-6} \text{ Pa}^{-1} \text{ s}^{-1}$	[86]
Condensation rate constant of methanol and water	k_{con}	10^3 s^{-1}	[86]
Methanol Henry's law constant	$k_{\text{H,m}}$	$0.096 \exp [0.04511 (T - 273)] \text{ atm}$	[71]
Saturation pressure of water	$\log_{10} (p_{\text{wv}}^{\text{sat}})$	$-2.1794 + 0.02953 (T - 273) - 9.1837 \times 10^{-5} (T - 273)^2 + 1.4454 \times 10^{-7} (T - 273)^3 \text{ atm}$	[71]
In-/through-plane dry effective diffusivity	$f^{\text{ip/tp}}$	$2.92 \times 10^{-2} \exp (3.8 \varepsilon) / 6.51 \times 10^{-3} \exp (5.02 \varepsilon)$	[6, 7, 86]
In-plane gas relative diffusivity (agdl/cgdl)	g_g^{ip}	$(1 - s)^{1.5} / (1 - s)^2$	[86]/[6–8]
Through-plane gas relative diffusivity (agdl/cgdl)	g_g^{tp}	$(1 - s)^{1.5} / (1 - s)^3$	[86]/[6–8]
In-/through-plane liquid relative diffusivity (agdl)	$g_l^{\text{ip/tp}}$	$s^{1.5}$	[86]
In-/through-plane absolute permeability	$K^{\text{ip/tp}}$	$2.52 \times 10^{-16} \exp (14.65 \varepsilon) \text{ m}^2 / 2.3 \times 10^{-16} \exp (12.51 \varepsilon) \text{ m}^2$	[86]
In-/through-plane gas relative permeability	$k_{\text{rg}}^{\text{ip/tp}}$	$(1 - s)^3$	[8, 86]
In-/through-plane liquid relative permeability	$k_{\text{rl}}^{\text{ip/tp}}$	s^3	[86]
In-/through-plane effective electrical conductivity	$\sigma^{\text{eff,ip/tp}}$	$48221 - 46729 \varepsilon \text{ S m}^{-1} / 6582 - 7229 \varepsilon \text{ S m}^{-1}$	[86]
Genuchten parameter of agdl (uncompr. sample)	$s_r / m / n / p_{c,b}$	$0.08 / 200 / 0.6 / 1.05 \times 10^5 \text{ Pa}$	[95]
Genuchten parameter of agdl (compr. sample)	$s_r / m / n / p_{c,b}$	$0.07 / 175 / 0.6 / 1.055 \times 10^5 \text{ Pa}$	[95]
Reference pressure	p_{ref}	$1.013 \times 10^5 \text{ Pa}$	[95]
Surface tension	σ	0.072 N/m	[9]
Contact angle of cgdl	$\theta_{c,\text{cgdl}}$	96°	[75]
GDL/BPP electrical contact resistance (graphite/metallic)	$R_c^{\text{gdl/bpp}}$	$2 (p_c^{\text{gdl/bpp}})^{-0.8} / 186 (p_c^{\text{gdl/bpp}})^{-1.09} \text{ m}\Omega \text{ cm}^2; p_c^{\text{gdl/bpp}} \text{ in MPa}$	[89]
Electrical contact resistance between the GDL-MPL diffusion medium and the membrane	$R_c^{\text{gdl/mem}}$	$\Pi \left[2 (p_c^{\text{gdl/mem}})^{-0.8} \right] \text{ m}\Omega \text{ cm}^2; \Pi \geq 0; p_c^{\text{gdl/mem}} \text{ in MPa}$	[89]

Table 4: Physicochemical and kinetic parameters of the local 1D model.

Parameter	Symbol	Value	Reference(s)
Ideal thermodynamic cell voltage	E_{cell}	$1.213 - 1.4 \times 10^{-4} (T - 298)$ $- \frac{0.5}{2} \frac{RT}{F} \log \left(\frac{p_{\text{C}}^{\text{ch}}}{1.013 \times 10^5} \right) \text{ V}$	[64]
MOR thermodynamic potential	U_{MOR}^0	0.03 V	[79, 84]
HER thermodynamic potential	U_{HER}^0	0 V	[79, 84]
MOR exchange current density	$i_{0,\text{m}}$	$94.25 \exp \left[\frac{35570}{R} \left(\frac{1}{353} - \frac{1}{T} \right) \right] \text{ A m}^{-2}$	[56]
ORR exchange current density	i_{0,O_2}	$0.04222 \exp \left[\frac{73200}{R} \left(\frac{1}{353} - \frac{1}{T} \right) \right] \text{ A m}^{-2}$	[51]
HER exchange current density	i_{0,H_2}	$2 \times 10^8 \exp \left[\frac{66000}{R} \left(\frac{1}{343} - \frac{1}{T} \right) \right] \text{ A m}^{-3}$	[79, 84]
MOR/ORR/HER transfer coefficient	$\alpha_{\text{m/O}_2/\text{H}_2}$	0.55/1/1	[57]/[71]/[79, 84]
Anode/cathode catalyst surface area per unit volume	$a_{\text{a/c}}$	$1.5 \times 10^5 \text{ m}^{-1} / 5.2 \times 10^5 \text{ m}^{-1}$	[89]
MOR electrochemical parameters	κ/λ	$7.5 \times 10^{-4} / 4.5 \times 10^{-3} \text{ mol m}^{-3}$	[57]/[89]
Reference oxygen concentration	$C_{\text{O}_2}^{\text{ref}}$	0.52 mol m ⁻³	[71]
Oxygen Henry's law constant	$k_{\text{H,O}_2}$	$\exp [(-666/T) + 14.1] / RT$	[71]
Effective diffusivity of methanol in the membrane	$D_{\text{ml,mem}}^{\text{eff}}$	$1.5 \times 10^{-10} \exp \left[2416 \left(\frac{1}{303} - \frac{1}{T} \right) \right] \text{ m}^2 \text{ s}^{-1}$	[75]
Electroosmotic drag coefficient of water	n_{d}^{w}	$2.9 \exp \left[1029 \left(\frac{1}{333} - \frac{1}{T} \right) \right]$	[67]
Effective protonic conductivity of the membrane	$\sigma_{\text{mem}}^{\text{eff}}$	$7.3 \exp \left[1268 \left(\frac{1}{298} - \frac{1}{T} \right) \right] \text{ S m}^{-1}$	[64]
Porosity of anode and cathode MPLs	$\varepsilon_{\text{ampl}}, \varepsilon_{\text{cmpl}}$	0.55	[89]
Porosity of anode and cathode CLs	$\varepsilon_{\text{acl}}, \varepsilon_{\text{ccl}}$	0.3	[71]
Contact angle of cathode MPL	θ_{cmpl}	96°	[75]
Contact angle of cathode CL	θ_{ccl}	120°	[75]
Permeability of cathode MPL	K_{cmpl}	$2.5 \times 10^{-13} \text{ m}^2$	[33]
Permeability of cathode CL	K_{ccl}	$1.5 \times 10^{-14} \text{ m}^2$	[33]

Figures

Figure 1: Schematic of the computational domains covered by the 2D anode/cathode GDL models and the local 1D model (MPLs, PEM, and CLs), showing the x - y coordinate system, cell temperature, T , methanol and oxygen concentrations at the GDL/channel interface, C_{ml}^{ch} and $C_{O_2}^{ch}$, anode and cathode channel saturation levels, s_a^{ch} and s_c^{ch} , and the notation used for the geometrical parameters. The inset shows the electrochemical reactions modeled at the anode and cathode catalyst layers.

Figure 2: Schematic of the 3D/1D MEA + 1D channel model used in the validation simulations. The 3D/1D MEA model is obtained from the extrusion of the 2D/1D across-the-channel model (Appendix A) in the along-the-channel direction (z -coordinate). 1D models for the anode and cathode channels (Appendix B) are coupled to the 3D/1D MEA model at each downstream station to account for the downstream variation of the different flow variables. The same GDL effective transport properties are assumed in the two orthogonal directions in the material x - z plane.

Figure 3: Computed polarization curves for different methanol feed concentrations, $\bar{C}_{\text{ml}}^{\text{ch},\text{in}} = 1$ and 2 M, as compared to the experimental data of Lu & Wang [29, Figs. 3 and 4]. Simulation parameters: $w_{\text{gdl}} = 1.46$ mm; $w_{\text{rib}} = 0.5$ mm; $\delta_{\text{agdl}}^{\text{u}} = \delta_{\text{cgdl}}^{\text{u}} = 260$ μm ; $\delta_{\text{mem}} = 50$ μm ; $\delta_{\text{ampl}} = \delta_{\text{cmpl}} = 20$ μm (assumed); $H_{\text{ch}} = 1.5$ mm; $L_{\text{ch}} = 2$ cm (estimated [29]); $T = 75$ $^{\circ}\text{C}$ (estimated [29]); $\bar{C}_{\text{ml}}^{\text{ch},\text{in}} = 1$ & 2 M; $\bar{C}_{\text{O}_2}^{\text{ch},\text{in}} = 7$ mol/ m^3 (estimated [29]); $\bar{u}_{\text{a,l}}^{\text{ch},\text{in}} = 0.0146$ m/s ($\xi_{\text{a}} = 200.7$ @ 200 mA/ cm^2 for $\bar{C}_{\text{ml}}^{\text{ch},\text{in}} = 1$ M, $\xi_{\text{a}} = 401.4$ @ 200 mA/ cm^2 for $\bar{C}_{\text{ml}}^{\text{ch},\text{in}} = 2$ M); $\bar{u}_{\text{c,g}}^{\text{ch},\text{in}} = 0.5$ m/s ($\xi_{\text{c}} = 31.5$ @ 200 mA/ cm^2); $\bar{p}_{\text{a,l}}^{\text{ch},\text{in}} = 0.1$ bar (assumed); $\bar{p}_{\text{c,g}}^{\text{ch},\text{in}} = 1$ bar (assumed); $\text{CR} = 20\%$ (assumed); $R_{\text{c}}^{\text{gdl/bpp}} = 0$ (assumed); $R_{\text{c}}^{\text{gdl/mem}} = 0$ (assumed); horizontally oriented cell, $\mathbf{g} \cdot \mathbf{n}_{\text{ch}} = 0$; $k_{\text{evp}} = 5 \times 10^{-6}$ Pa $^{-1}$ s $^{-1}$, $k_{\text{con}} = 5 \times 10^3$ s $^{-1}$ (assumed). Other parameters as in Tables 1, 3, and 4.

Figure 4: Computed limiting current density versus methanol feed concentration for various total methanol flow rates, $Q_{a,l}^{ch,in,T} = 1, 2.5, 5, 10, \text{ and } 25 \text{ ml/min}$, as compared to the experimental data of Xu et al. [16, Fig. 5(b)]. The methanol flow rates prescribed in the single-channel simulations were equal to $Q_{a,l}^{ch,in} = Q_{a,l}^{ch,in,T}/15$ in order to account for the flow distribution in the 15 channels of the parallel flow field [16, 59]. Simulation parameters: $w_{gdl} = 1 \text{ mm}$; $w_{rib} = 0.5 \text{ mm}$; $\delta_{agdl}^u = \delta_{cgdl}^u = 300 \text{ } \mu\text{m}$ (assumed); $\delta_{ampl} = \delta_{cmpl} = 0$; $H_{ch} = 1 \text{ mm}$; $L_{ch} = 3 \text{ cm}$; $T = 75 \text{ } ^\circ\text{C}$; $\bar{C}_{ml}^{ch,in} = 0.125 - 0.75 \text{ M}$; $\bar{C}_{O_2}^{ch,in} = 7.35 \text{ mol/m}^3$; $\bar{u}_{a,l}^{ch,in} = 0.001 - 0.025 \text{ m/s}$ ($Q_{a,l}^{ch,in} = (1 - 25)/15 \text{ ml/min}$, $\xi_a = 0.67 - 100.7 \text{ @ } 200 \text{ mA/cm}^2$); $\bar{u}_{c,g}^{ch,in} = 0.22 \text{ m/s}$ ($Q_{c,g}^{ch,in} = 13.3 \text{ ml/min}$, $\xi_c = 5.25 \text{ @ } 200 \text{ mA/cm}^2$); $\bar{p}_{a,l}^{ch,in} = 1 \text{ bar}$; $\bar{p}_{c,g}^{ch,in} = 1 \text{ bar}$; $CR = 10\%$ (assumed); $R_c^{gdl/bpp} = 0$; $R_c^{gdl/mem} = 0$; horizontally oriented cell, $\mathbf{g} \cdot \mathbf{n}_{ch} = 0$; $a_a = 2 \times 10^6 \text{ m}^{-1}$ (estimated [59]). Other parameters as in Tables 1, 3, and 4.

Figure 5: Computed along-the-channel distributions of (a) methanol concentration, $\bar{C}_{ml}^{ch}(z)$, (b) gas-void fraction, $1 - \bar{s}_a^{ch}(z)$, and (c) current density, $I(z)$, for various total methanol flow rates, $Q_{a,l}^{ch,in,T} = 1, 2.5, 5, 10$, and 25 ml/min, at $V_{cell} = 0.25$ V corresponding to a 0.5 M methanol solution. The markers are plotted at the computational centers of the 20 stations in which the 3D/1D MEA + 1D channel model was divided in the along-the-channel direction. See caption to Fig. 4 for further details.

Figure 6: Computed along-the-channel distributions of (a) oxygen concentration, $\bar{C}_{O_2}^{ch}(z)$, and (b) current density, $I(z)$, for various air flow rates, $Q_{c,g}^{ch,in} = 3, 5$, and 10 ml/min, as compared to the experimental data of Sauer et al. [103, Fig. 8] (see inset in (b)). The output current density is approximately equal to 20 mA/cm² in all the cases ($I = 16.5$ for 3 ml/min, $I = 22.8$ for 5 ml/min, and $I = 22.2$ for 10 ml/min), while the cell voltage, V_{cell} , is indicated in round brackets. A liquid-feed DMFC operating in bifunctional regime with both galvanic and electrolytic regions is observed at $Q_{c,g}^{ch,in} = 3$ and 5 ml/min. The markers are plotted at the computational centers of the 20 stations in which the 3D/1D MEA + 1D channel model was divided in the along-the-channel direction. Simulation parameters: $w_{gdl} = 1$ mm; $w_{rib} = 0.5$ mm; $\delta_{agdl}^u = \delta_{cgdl}^u = 350$ μ m (assumed); $\delta_{ampl} = \delta_{cmpl} = 20$ μ m (assumed); $H_{ch} = 1$ mm; $L_{ch} = 10$ cm; $T = 80$ $^{\circ}$ C; $\bar{C}_{ml}^{ch,in} = 1$ M; $\bar{C}_{O_2}^{ch,in} = 7.15$ mol/m³ (estimated [103]); $\bar{u}_{a,l}^{ch,in} = 0.0017$ m/s ($Q_{a,l}^{ch,in} = 0.1$ ml/min, $\xi_a = 16.1$ @ 20 mA/cm²); $\bar{u}_{c,g}^{ch,in} = 0.05 - 0.1667$ m/s ($Q_{c,g}^{ch,in} = 3 - 10$ ml/min, $\xi_c = 2.3 - 7.66$ @ 20 mA/cm²); $\bar{p}_{a,l}^{ch,in} = 1$ bar; $\bar{p}_{c,g}^{ch,in} = 1$ bar; CR = 30% (assumed); $R_c^{gdl/bpp} = 0$ (assumed); $R_c^{gdl/mem} = 0$ (assumed); horizontally oriented cell, $\mathbf{g} \cdot \mathbf{n}_{ch} = 0$ (assumed). Other parameters as in Tables 1, 3, and 4.

Figure 7: Computed cell performance as a function of oxygen concentration at the GDL/channel interface, $C_{O_2}^{ch} = 1 - 5$ mol/m³, for various methanol concentrations, $C_{ml}^{ch} = 1, 2,$ and 3 M: (a) and (b) output power density, P , and fuel utilization, $FU = (I + I_p)/I$, at $V_{cell} = 0.25$ V; and (c) polarization curves for different oxygen concentrations at the GDL/channel interface, $C_{O_2}^{ch} = 2, 3.5,$ and 5 mol/m³ ($\xi_c = 0.7, 1,$ and 1.75). Other operating conditions as in Table 2.

Figure 9: Variation of the output current density with GDL compression ratio at $V_{\text{cell}} = 0.25 \text{ V}$ for Graphite (G) and Metallic (M) bipolar plates, and different reactant concentrations at the GDL/channel interface: (a) fixed oxygen concentration, $C_{\text{O}_2}^{\text{ch}} = 3.5 \text{ mol/m}^3$ ($\xi_c = 1$), and various methanol concentrations, $C_{\text{ml}}^{\text{ch}} = 1, 2$, and 3 M ; and (b) fixed methanol concentration, $C_{\text{ml}}^{\text{ch}} = 3 \text{ M}$, and various oxygen concentrations, $C_{\text{O}_2}^{\text{ch}} = 2, 3.5$, and 5 mol/m^3 ($\xi_c = 0.7, 1$, and 1.75). The optimum compression ratios that maximize the cell performance are indicated by green stars, and labeled A, B & C for the different operational parameters varied in each subplot. Other operating conditions as in Table 2.

Figure 10: Computed polarization curves at various GDL compression ratios, $\text{CR} = 10 - 50\%$, for the metallic bipolar plate and various of the operational cases examined in Fig. 9: (a) $C_{\text{ml}}^{\text{ch}} = 1 \text{ M}$, $C_{\text{O}_2}^{\text{ch}} = 3.5 \text{ mol/m}^3$ ($\xi_c = 1$); (b) $C_{\text{ml}}^{\text{ch}} = 3 \text{ M}$, $C_{\text{O}_2}^{\text{ch}} = 3.5 \text{ mol/m}^3$ ($\xi_c = 1$); (c) $C_{\text{ml}}^{\text{ch}} = 3 \text{ M}$, $C_{\text{O}_2}^{\text{ch}} = 2 \text{ mol/m}^3$ ($\xi_c = 0.75$); (d) $C_{\text{ml}}^{\text{ch}} = 3 \text{ M}$, $C_{\text{O}_2}^{\text{ch}} = 5 \text{ mol/m}^3$ ($\xi_c = 1.75$). Other operating conditions as in Table 2.

Figure 11: (a) Variation of the average current density, I , in the region under the rib (solid lines) and under the channel (dashed lines) as a function of the multiplicative factor, Π , of the electrical contact resistance between the GDL-MPL diffusion medium and the membrane, $R_c^{\text{gdl}/\text{mem}}$. (b) Local current density distribution, $i(x)$, corresponding to some specific values of Π ; the region under the rib is indicated with a grey background. Results are shown for different cell voltages, $V_{\text{cell}} = 0.4, 0.25$, and 0.1 V. $R_c^{\text{gdl}/\text{mem}} = 2\Pi(p_c^{\text{gdl}/\text{mem}})^{-0.8} \text{ m}\Omega \text{ cm}^2$. The methanol and oxygen concentrations are equal to $C_{\text{ml}}^{\text{ch}} = 2 \text{ M}$ and $C_{\text{O}_2}^{\text{ch}} = 3.5 \text{ mol/m}^3$ ($\xi_c = 1$), respectively. Other operating conditions as in Table 2.

Figure 12: Computed cell performance as a function of methanol concentration at the GDL/channel interface, $C_{ml}^{ch} = 0.1\text{--}6$ M, and cell temperature, $T = 30\text{--}80$ °C: (a) and (b) output power density, P , and parasitic current density, I_p , at $V_{cell} = 0.25$ V, and (c) polarization curves corresponding to two specific methanol concentrations, $C_{ml}^{ch} = 1$ and 5 M, and various cell temperatures, $T = 30, 45, 65$, and 80 °C. The oxygen concentration is equal to $C_{O_2}^{ch} = 6$ mol/m³ ($\xi_c = 3.5$). Other operating conditions as in Table 2.

Figure 13: Variation of the output power density with methanol concentration at the GDL/channel interface, $C_{ml}^{ch} = 1 - 4$ M, at $V_{cell} = 0.25$ V for various (a) anode gas coverage factors, $1 - s_a^{ch} = 0.1, 0.3$, and 0.6 , and (b) cathode saturation levels, $s_c^{ch} = 0.2, 0.4$, and 0.6 . The oxygen concentration is equal to $C_{O_2}^{ch} = 6$ mol/m³ ($\xi_c = 3.5$). Other operating conditions as in Table 2.