Impact of Ionomer Content on Proton Exchange Membrane Fuel Cell Performance

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Abstract

The effect of Nafion ionomer content on performance of a PEM fuel cell operated with home-made anodic and cathodic electrodes fabricated from a novel MOF derived Pt-based electrocatalyst was investigated via numerical simulation and experimental measurement. First, the parameter sensitivity analysis was performed to identify the most influential parameters of the model. Then, these parameters were calibrated for different fuel cell designs investigated in the current study by employing the corresponding experimental data. Afterward, the calibrated model was used to examine the impact of Nafion content in the catalyst layer of home-made electrodes. Finally, the qualitative trend predicted by this model was experimentally surveyed by varying the Nafion content between 10-50 wt.% in the catalyst layer of home-made electrodes. At the anode side, the performance of home-made electrode in a PEM fuel cell demonstrated small dependency on Nafion content. For the cathodic home-made electrode, Nafion content was found to affect the PEM fuel cell performance more strongly. Although the model could correctly capture the impact of Nafion content on calculated polarization curves, the model predicted optimum values significantly deviate from the experimental results. This was related to the several simplifications made during model development.

Keywords: Catalyst Layer, Experimental Validation, Nafion Content, Numerical Simulation, PEM Fuel Cell, Polarization Curve

1 Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered a promising alternative to internal combustion engines. Large-scale commercialization of PEMFCs, however, is strongly impeded due to the cost issues mainly related to the use of platinum (Pt) electrocatalyst within catalyst layers [1, 2].
Effective non-PGM catalysts that could provide both high activity comparable to Pt and long-term stability under practical fuel cell operating conditions have not yet been achieved. Therefore, for the moment, Pt or Pt alloys are remaining as the only realistic choice [3-5]. In this context, it is vital to develop synthetic approaches toward producing more efficient Pt-based catalysts with a regular structure and controlled properties. In addition, optimizing the composition and structure of catalyst layers could enhance Pt utilization and hence, reduce the Pt content in the electrodes of PEMFCs.

Recently, new Pt-based electrocatalysts were prepared through a novel approach, i.e., by pyrolytic transformation of the Pt containing metal organic framework (MOF) [6]. To the best of the authors’ knowledge, this was the first report on employing MOF as the sole precursor to fabricate Pt-based electrocatalyst. These electrocatalysts were used to prepare ink solutions containing 20 wt.% of Nafion ionomer (based on dry electrocatalyst) in their formulation. The catalytic performance of the anodic and cathodic electrodes prepared from such inks (home-made electrodes), were subsequently examined against a commercial electrode in a single PEM fuel cell. For the same Pt loading of 0.5 mg cm$^{-2}$, the home-made electrodes revealed performances comparable to the commercial electrode. However, the results demonstrate a potential to improve the performance via ink modification (varying Nafion ionomer content).

The effect of Nafion content in catalyst layers on the overall fuel cell performance has been investigated through experimental studies [7, 8]. Passalacqua et al. [9] studied the impact of the Nafion content (14 to 66 wt.%) on the overall performance of a single cell PEM fuel cell with low platinum loading (0.1 mg cm$^{-2}$). They found a dependency between PEM fuel cell performance and Nafion ionomer content in the electrodes. Later, Sasikumar et al. [10] searched for a relationship between optimum Nafion content and Pt loading in the catalyst layer and found that the optimum Nafion content is determined by Pt loading. Different formulations have been applied to prepare the ink solution in PEMFCs throughout the literature. For instance, ratios between the masses of the catalyst and Nafion ionomer [11, 12], Pt and Nafion ionomer [10, 13] or carbon and Nafion [14, 15] have been used to define the catalyst ink formulation. These formulations are mainly reported for standard Pt/C catalyst (20-40 wt.% Pt supported on Vulcan XC72 carbon support), but some other works have investigated the optimum ink formulation for other types of electrocatalysts or carbon supports [16-18].

Computational modeling has also been used to investigate the impact of Nafion ionomer content on the catalyst layer properties and Pt utilization. Various mathematical models have been developed to describe catalyst layers in PEMFCs including macro-homogeneous models [19, 20], thin-film models [21, 22], agglomerate models [23-29] and pore-scale models [30-32]. Employing the agglomerate model, Kamarajugadda and Mazumder [25] demonstrated the existence of an optimal fuel cell performance with changing ionomer volume fraction in the catalyst layer. Considering spherical agglomerate structure for the catalyst layer, Xing et al. [33] used a two dimensional, across the channel, two-phase flow model to optimize the initial dry ionomer content in the cathode catalyst layer for an enhanced PEM fuel performance. They considered the effect of ionomer swelling on the catalyst layer porosity and oxygen mass transport resistance. According to their results, the best fuel cell performance could be achieved at initial dry ionomer volume fraction of 10%, corresponding to 0.3 mg cm$^{-2}$.

In summary, earlier experimental measurements and numerical simulations both showed that Nafion content in catalyst layer has a significant impact on the PEMFC performance and Pt
electrocatalyst utilization. The impact of Nafion content on the performance of PEMFC operated with home-made electrodes prepared from the novel Pt-based MOF derived electrocatalysts presented in [6] has however not yet been performed. Such study could lead to more effective electrodes that subsequently would improve the fuel cell performance.

Hence, in this paper, the main objective is to study the effect of Nafion ionomer content on the performance of a single cell PEM fuel cell operated with home-made electrodes fabricated from a novel MOF derived Pt-based electrocatalyst [6]. Such study could eventually enhance the fuel cell performance by providing higher currents densities \(i\) at a given operating voltage \(V\). The analyses presented in this paper are performed by comparing numerical simulations tools results and experimental measurements.

2 Description of the Fuel Cell Device

The fuel cell device investigated in this paper is illustrated in Figure 1. More specifically, in Figure 1(a) it can be seen that two end plates enclose current collectors, bipolar plates, gasket layers, and a membrane electrode assembly (MEA). The end plates are used to maintain a compressive stress on the system, which provides good contacts between inner adjacent layers of the fuel cell. Collector plates allow the electrical current produced by the fuel cell to be directed toward external devices. Bipolar plates contain grooved channels in which the reactants and products can flow (see Figure 1(b)). Moreover, the end plates, current collector and bipolar plates include internal pathways (not presented in Figure 1) in order to allow reactant gases and products to reach and leave the grooved channels. The gasket layers encase the MEA and are used to prevent gas leakage from the fuel cell. The different layers that constitute the MEA are illustrated in Figure 1(c) and are identified as layers II to VI. The MEA is made of a proton conductive (ionomer) membrane (layer IV) bounded by two electrode layers (cathode and anode sides). These electrodes are made of a porous and electrically conductive medium (the diffuser, layers II and VI) on which a thin layer of electrocatalyst (layers III and V) is deposited. These electrocatalyst layers are in contact with the membrane, and are made of a mixture of Pt catalyst and Nafion ionomer, which allows transport of proton from the reaction sites (on Pt particles) to the membrane layer.

The exact geometry of channels grooved on the bipolar plates is presented in Figure 1(b). The fluids flow within end plates, current collector and bipolar plates through internal pathways, then reach the grooved channels by the entry site “In” (see Figure 1(b)), and then leave the grooved channels by the exit site “Out” (see Figure 1(b)). Notice that the MEA is next to the channel on a well-defined effective area of size \(1.4 \times 1.4 \text{ cm}^2\); in other word, the parts of the channel that are not directly adjacent to the MEA do not contribute to the electrochemical reactions (see Figure 1(b)).

Overall, in the fuel cell illustrated in Figure 1(a), hydrogen (with water vapour) arrives via the end plate entry on the anode side, then it flows through the channels and diffuser, and finally it reacts in the catalyst layer to become protons and electrons. The protons generated move through the ionomer phase that is present in the catalyst layers and in the membrane, so as to reach the catalyst in the cathode. The electrons reach the anode collector and circulate in an external circuit so as to reach the cathode collector and then the cathode catalyst. On the other
side of the fuel cell, oxygen (with water vapour) enters the fuel cell via the cathode end plate entry, then it flows through the cathode channels and diffuser, and it finally reacts with protons and electrons in the cathode catalyst layer, which produces water. To summarize, the fuel cell receives hydrogen, oxygen and water, and produces water, heat and electricity.

2.1 Description of the Three Designs of Interest

In the current study, three variants of the general fuel cell design described above are investigated (see Figure 2). They correspond to: (i) a fuel cell including a commercial electrode for both the anode and cathode sides (Figure 2(a)); (ii) a fuel cell including a home-made electrode (Pt-based electrocatalyst derived from MOF precursor) at the anode side and the commercial electrode at the cathode side (Figure 2(b)); and (iii) a fuel cell including the commercial electrode at the anode side, while the home-made electrode is used at the cathode side (Figure 2(c)).

Notice that the overall design of these three variants are identical to that shown in Figure 1, i.e., the size and geometry of the end plates, collectors, bipolar plates, gasket and MEA area (1.4 × 1.4 cm²) remain unchanged. The geometrical differences between these designs occur, however, in the thickness of the electrodes inner layers (L₁₁₁, L₁₁₁¹, L₆, and L₆¹); the value of these parameters are reported for each design in Figure 2, and were obtained from the supplier (commercial electrodes) and from experimental measurement (home-made electrode).

2.2 Description of the MEAs

MEAs that are used in the three designs described in Section 2.1 are assembled from commercial and/or home-made electrodes and a Nafion NRE-212 membrane. The commercial electrode (ELAT® V2.1, Single Sided Coating on TGPH-060, Pt loading (mₚ) of 0.5 mg cm⁻²) is provided by BASF and used at either anode or cathode side without any further processing.

The home-made electrodes are prepared by the author’s research team [6]. The electrocatalyst used in the home-made electrodes were prepared through pyrolytic transformation of the Pt-based MOF precursor. More details on synthesis of the parent Pt-MOF and its pyrolytic transformation to the electrocatalyst precursor are reported in [6]. Previously, employing a range of thermolysis temperature (700-1050 °C), different electrocatalysts were prepared. However, in the current study only the most promising electrocatalyst (T thermolysis = 950 °C) is considered.

The catalyst ink is prepared by ultrasonic blending of the electrocatalyst with Nafion solution (5 wt.%, Sigma-Aldrich) in isopropyl alcohol for 2 h. This ink is then applied to a commercial GDL (Toray carbon paper, TGP-H-060, BASF) by successive brushing until the Pt loading (mₚ) of ~ 0.5 mg cm⁻² is reached.

2.3 Description of the Operating Condition
Experimental conditions under which the PEM fuel cell performance is conducted on a test station (Fideris TM Hydrogen Test Kit TM) to obtain the polarization curves, are provided in Table 1. Hydrogen and air, humidified at 80 °C, are used as fuel and oxidant gasses at the anode and cathode, respectively. In addition, the parameters reported in Table 1 are the operational parameters used in the numerical model employed in the current study.

3 Mathematical Modeling and Numerical Strategy

In upcoming sections of the paper, fuel cell performance is calculated by using numerical simulations. The mathematical model is presented in the Section 3.1, and the numerical tools are presented in Section 3.2.

3.1 Mathematical Model

Strictly speaking, the fuel cell presented in Section 2 (Figure 1) involves three-dimensional transport phenomena, temperature gradient, two-phase flow (liquid and vapour water) and complex water transport phenomena through the membrane. However, the purpose of this paper is not to obtain precise numerical data that represent exactly the physical fields throughout the fuel cell, but rather to highlight the main trends of the fuel cell performance with respect to several important variables. Therefore, a simplified mathematical model that was developed in a previous work [34] was adapted to the present work.

The model used in this work considers a two-dimensional (along the channels) section of the PEM fuel cell and consists of seven subdomains (layers I to VII) as shown in Figure 3. Two-dimensional “along the channel” geometry has often been used in the literature for fuel cell numerical modeling. The height $H$ shown in Figure 3 corresponds to the total length of the serpentine shown in Figure 1(b) that is adjacent to the MEA (i.e., the length of the channel included in the $1.4 \times 1.4 \text{ cm}^2$ rectangle). In another word, the height $H$ used in numerical simulation represents the serpentine geometry applied in the experimental single cell set up. The model implements: (i) a set of conservation equations for mass, momentum, species and charges, (ii) kinetic expressions for chemical reactions, (iii) expressions for calculating the required thermodynamic properties for ideal gases (iv) boundary conditions, (v) thermophysical properties, (vi) geometry of the domain, and (vii) operating conditions of the fuel cell. The places of these parameters in the model are described in a previous work [34].

The fuel cell is assumed to operate at steady-state with a uniform operating temperature (in the domain) and a uniform electric potential in the solid phase of each electrode. Electric potential varies within the ionomer phases that is present in the membrane (layer IV) and electrocatalyst layers (layer III and V), see Figure 3. More specifically, that potential drives the motions of dissolved protons $H_1^\text{(d)}$ in the ionomer phase. The gas mixture in the gas channels is presumed to behave as an ideal gas and the flow is assumed to be laminar due to the small velocities involved. This model only considers the gaseous water transport and hence, it does not include the flooding effect and the resulting sharp potential drop that may happen at higher current densities ($\geq 1 \text{ A cm}^{-2}$). Nonetheless, the presence of liquid water is taken into account implicitly and by applying an effective porosity value in the GDL (as proposed in Ref. [35]) which
is smaller than its dry porosity value provided by the supplier. More details about that initial model may be found in [34].

In this paper, fuel cell performance has to be obtained for various Nafion content and operating conditions (i.e., various temperature and pressure values). As a consequence, the mathematical model described in [34] was improved in the following way:

(i) While in the previous study [34], the gas permeability in the catalyst layers (layers III and V) and gas diffusion layers (GDLs), layers II and VI, possessed a constant given value \( K_{\text{porous}} \), in the current study, the gas permeability in the gas diffusion layers \( K_{\text{GDL}} \) differs from the gas permeability in the catalyst layers \( K_{\text{CL}} \). The actual value for \( K_{\text{GDL}} \) is available from the supplier technical specifications (see Table 2). The gas permeability in the catalyst layers is now calculated using the Kozeny-Carman equation [27, 36] as follows:

\[
K_{\text{CL}} = \beta \frac{\varepsilon_{\text{CL}}^3}{(1-\varepsilon_{\text{CL}})^2} \quad (1)
\]

where \( \beta \) is a constant determined from GDL properties and \( \varepsilon_{\text{CL}} \) is the porosity of catalyst layers.

(ii) In the previous study [34], the porosity of the catalyst layers (layers III and V) and gas diffusion layers (layers II and VI) were assumed to possess a constant given value of \( \varepsilon_{\text{porous}} \), however, in the current study, the porosity in the gas diffusion layers \( \varepsilon_{\text{GDL}} \) is different from the porosity of the catalyst layers \( \varepsilon_{\text{CL}} \). \( \varepsilon_{\text{GDL}} \) is provided by the supplier and is given in Table 2. The porosity of the catalyst layer \( \varepsilon_{\text{CL}} \) is now expressed as a function of the \( \varepsilon_{\text{GDL}} \) and catalyst layer properties, according to the following equation [37]:

\[
\varepsilon_{\text{CL}} = \varepsilon_{\text{GDL}} (1 - \varepsilon_{\text{m,catalyst}}) - \frac{m_{\text{Pt}}}{L_{\text{CL}} f} \left( \frac{f}{\rho_{\text{Pt}}} + \frac{1-f}{\rho_{\text{C}}} \right) \quad (2)
\]

where \( m_{\text{Pt}} \) is the Pt mass loading per unit area of the catalyst layer, \( L_{\text{CL}} \) is the catalyst layer thickness (either \( L_{\text{III}} \) or \( L_{\text{V}} \)), \( f \) represents the mass percentage of Pt in the Pt/C catalyst [6], \( \rho_{\text{Pt}} \) and \( \rho_{\text{C}} \) are the mass densities of the Pt and carbon black, respectively [37].

(iii) Binary mutual diffusion coefficients between two species \( x \) and \( y \) are now expressed as functions of the operating temperature and pressure according to the following equation [38]:

\[
D_{xy}(T, P) = D_{xy}^{\text{ref}} \left( T^{\text{ref}}, P^{\text{ref}} \right) \times \left( \frac{T}{T^{\text{ref}}} \right)^{1.5} \left( \frac{P^{\text{ref}}}{P} \right) \quad (3)
\]

(iv) The open circuit potential \( V_{\text{OC}} \) at the cathode is now calculated according to the following equation [39]:

\[
V_{\text{OC}} = 0.00257 T + 0.2329 \quad (4)
\]

where \( T \) is in kelvin and \( V_{\text{OC}} \) is in volts. It is worth mentioning that \( V_{\text{OC}} \) as appears in Eq. (4) is not the real open circuit potential of cathode which according to the Nernst equation is also a function of oxidant concentration. Indeed, \( V_{\text{OC}} \) only represents the constant term in the expression of the open circuit potential as a function of temperature. The concentration-dependent term of the \( V_{\text{OC}} \) that possesses a logarithmic form can then be extracted from
the exponent in the Butler-Volmer equation and can then become the concentration term \( \frac{C_{O_2}}{C_{O_2}^{ref}} \) in front of the exponent in Eq. (7) (Section 4.1).

(v) Finally, the temperature dependency of the pre-exponential coefficient \( a_{j_0,c}^{ref} (T) \) in the electrochemical expression of the cathode reaction is estimated from Eq. (5) [39]:

\[
a_{j_0,c}^{ref} (T) = a_{j_0,c}^{ref} (353 K) \cdot \exp[0.014189(T - 353)]
\]  

(5)

By including Eq. (1) in the model, it is now possible to take into account the impact of the volume fraction available for gas flow in the catalyst layer (\( \varepsilon_{CL} \)) on the momentum equation via the gas permeability (\( K_{CL} \)). Furthermore, by adding Eq. (2) in the model, it is now possible to explicitly include the impact of Nafion content in the catalyst layer (\( \varepsilon_{m,catalyst} \)) on the volume fraction available for gas flow (\( \varepsilon_{CL} \)). In other words, the model is able to capture the impact of the catalyst layer Nafion content in the catalyst layer. Finally, including Eqs. (3)-(5) in the model allows to capture the impact of the operating pressure and temperature on the PEM fuel cell performance.

3.2 Numerical Methodology

The fuel cell geometry and modified mathematical method described in Section 3.1 have been implemented in a finite element software [40, 41]. The domains were divided in a structured mesh of rectangular elements, and physical fields were calculated between nodes by using quadratic Lagrange interpolation.

The number of rectangular elements used in numerical simulations is defined by the number of nodes used along each of the boundaries demonstrated in Figure 3. For the design using only commercial electrodes (introduced in Figure 2(a)), there were 50 nodes along the y-axis present in Figure 3; 20 nodes along the x-axis in subdomains I and VII; 35 nodes along the x-axis in subdomains II and VI; 63 nodes along the x-axis in subdomains III and V; and 20 nodes along the x-axis in subdomain IV. For the design that includes the home-made electrode on the anode side (introduced in Figure 2(b)), the number of nodes along the x-axis for subdomains of II and III was changed to 19 and 76, respectively. Similarly, for the design that includes the home-made electrode on the cathode side (introduced in Figure 2(c)), the nodes number along the x-axis was changed to 76 and 19 for subdomains of V and VI, respectively.

Considering the dimensions of the domains, it should be noticed that the rectangular elements of the mesh are indeed extremely slender. Nevertheless, the commercial software used here has already proven its ability to handle such elements in previous studies [34, 42]. A solver of the type “fully coupled” was selected in the finite element software [40], and convergence is declared when the relative error was smaller than \( 10^{-6} \). With the meshes described above, it was verified that the value of the electric current density \( i \) changed by less than 0.5% when the number of elements was doubled in each direction. Hence, the meshes described above are considered adequate to declare mesh independence.

4 Sensitivity Analysis
Mathematical PEM fuel cell models of different complexity involve different constants (usually called “parameters”) to calculate the polarization curves. These parameters can be classified as geometrical (design) parameters, operational parameters (temperature, pressure, humidity, flow rate, etc.), physical parameters (porosity, permeability, etc.) and electrochemical parameters (exchange current density, transfer coefficient, etc.) [43]. While some of these parameters can be measured directly [44, 45] and used in numerical models, others could only be assumed or estimated with some degree of uncertainty. The values of these undetermined and therefore adjustable parameters may have negligible, moderate, or important impact on the simulations results. Hence, it is important to identify the most influential undetermined parameters and then obtain accurate values for them, in order to develop a numerical model that correctly predicts the performance of the fuel cell. The undetermined parameters of the model presented in this work will be investigated in the following section.

4.1 Description of the Parameters

Tables 1-3 list the operational, physical and electrochemical and geometrical parameters of the mathematical PEM fuel cell model described in Section 3 which are considered to be accurately known. Other model parameters that remain undetermined and required to be estimated for the fuel cell investigated in this paper are listed in the first column of Table 4. These parameters are: the exchange current density multiplied by the specific surface area \((a_{j0,a}^{ref})\) at the anode side, the transfer coefficient \((\alpha_a)\) at the anode side, exchange current density multiplied by the specific surface area \((a_{j0,c}^{ref} (353 K))\) at the cathode side, the transfer coefficient \((\alpha_c)\) at the cathode side, and membrane protonic conductivity \((\sigma_m)\).

The first four parameters listed above are related to the electrochemical reactions that occur in the catalyst layers; in other words, they appears in the kinetic expressions of the mathematical model, i.e.,

\[
r_a = a_{j0,a}^{ref} (C_{H_2}/c_{H_2}^{ref})^{1/2} ((\alpha_a + \alpha_c)F\eta/RT) \quad (6)
\]

\[
r_c = -a_{j0,c}^{ref} (C_{O_2}/c_{O_2}^{ref}) (\exp(-\alpha_c F\eta/RT) - \exp(\alpha_c F\eta/RT)) \quad (7)
\]

where the dependence of \(a_{j0,a}^{ref} (T)\) with respect to temperature is developed in Eq. (5). These equations represent a simplified version of the general Butler-Volmer expression adopted in the model to determine the rate of oxidation \((r_a)\) and reduction \((r_c)\) reactions occurring at the anode and cathode electrodes [34].

The values of the four electrochemical parameters \(a_{j0,a}^{ref}\), \(a_{j0,c}^{ref} (353 K)\), \(\alpha_a\) and \(\alpha_c\) depend on the microscopic/nanoscopic characteristics of the electrocatalyst, and as a consequence, they can only be obtained from experimental measurement. Finally, the membrane conductivity, \(\sigma_m\), strongly depends on the average water content of the fuel cell investigated [46], and hence, on the global design of the fuel cell. Therefore, the membrane conductivity was identified as an undetermined parameter.
4.2 Parametric Analysis

Polarization curves are calculated by varying only one parameter at a time and keeping the rest of the parameters constant at their base values. These base values are reported in Table 4 and were used in our previous work [34] for fuel cell numerical simulations. The variation range of these parameters, also presented in Table 4, is selected based on their maximum and minimum values reported in literature.

Figures 4(a) and (b) display the effect of $a_{f_0,a}^{\text{ref}}$ and $a_{f_0,c}^{\text{ref}}$ (353 K) on the calculated polarization curves. As can be seen from these figures, while $a_{f_0,c}^{\text{ref}}$ (353 K) (Figure 4(b)) demonstrates significant impact on the predicted values of V-I in all the current density range, $a_{f_0,a}^{\text{ref}}$ (Figure 4(a)) mainly affects the model predictions in the medium current density range. In other words, at lower overpotentials, the activation resistance dominates the fuel cell performance, and the cathode exchange current density has more influence, which is expected due to the limiting effect of cathode reduction reaction. Indeed, the cathode oxygen reduction reaction (ORR) is several orders of magnitude slower than the anode hydrogen oxidation reaction (HOR), and is thus the limiting factor of the fuel cell performance [47] at low overpotential. In addition, Figure 4(a) reveals that at some point, increasing $a_{f_0,a}^{\text{ref}}$ values ($\geq 5 \times 10^{10}$ A m$^{-3}$) has negligible impact on the calculated values of the polarization curve; in other words, the limiting effect of the anode vanishes and the polarization becomes mainly dictated by other losses.

It should be noticed that the value of $a_{f_0,a}^{\text{ref}}$ (353 K) doesn’t change the slope of the curves in the linear region of the polarization curves, dominated by internal resistance (see Figure 4(b)), which is in line with earlier works [48, 49]. On the other hand, the value of $a_{f_0,a}^{\text{ref}}$ affects the slope of the linear portion of the polarization curves, especially for values $< 5 \times 10^{9}$ A m$^{-3}$. Such a difference in behaviour between $a_{f_0,a}^{\text{ref}}$ and $a_{f_0,c}^{\text{ref}}$ (353 K) can be explained by comparing the form of Eqs. (6) and (7). Indeed, a proportional dependence between the reaction rate and the overpotential $\eta$ is used in the electrochemical expression of $r_a$ in the anode (Eq. (6)), while an exponential dependence was used in Eq. (7) for $r_c$ at the cathode, which explains the different trends of Figure 4(a) and (b). Linear dependency for the anode side has been used in previous works [34, 50]. Overall, it can be concluded that the values of $a_{f_0,a}^{\text{ref}}$ and $a_{f_0,c}^{\text{ref}}$ (353 K) have a strong influence on the calculated polarization curves.

The effect of transfer coefficients $\alpha_a$ and $\alpha_c$ on the calculated polarization curves are illustrated in Figures 4(c) and (d), respectively. As can be seen from these figures, $\alpha_c$ has a significant effect on the polarization curves, whereas $\alpha_a$ has negligible impact. This is again related to the electrochemical expressions applied for $r_a$ and $r_c$ in the model.

The last parameter involved in the sensitivity analysis of the model is the membrane conductivity ($\sigma_m$). The protonic conductivity of a membrane is a function of membrane water content and temperature [46]. Since in this study the liquid water transport is however not explicitly considered, the electrolyte phase is postulated to have a constant and uniform conductivity. Assuming constant values for $\sigma_m$ was found adequate to present a qualitative description of the fuel cell performance [48]. In Figure 4(e), the parametric analysis reveals that variations of $\sigma_m$ in the range of values typically found in the literature, yield important changes
of the polarization curves. Moreover, it can be confirmed that larger values of membrane conductivity lead to higher potential values at a given current density, and hence to a better fuel cell performance [51].

To summarize this sensitivity analysis, it could first be stated that the influence of transfer coefficient of the anode reaction $\alpha_a$ on the polarization curves predicted by the model is very small. Hence, the base value reported in Table 4 will be assigned to this parameter for the rest of the analysis. However, the values of $\alpha_{c}$, $a_{j_0}^{ref}$, $a_{j_0}^{ref} (353 K)$, $\sigma_m$, and $\sigma_{m}$ were shown to influence significantly the model predicted fuel cell performance over their respective range of accepted literature values. Therefore, these four parameters will be adjusted in the following steps for the model calibration.

Finally, it is informative to notice that most influential parameters identified by the sensitivity analysis in this paper are similar to those obtained previously [48]; However, the authors of this reference used a much more complex model involving three-dimensional, two-phase, non-isothermal simulations. Hence, the simplification used in the current model proved to correctly capture the essential phenomena in the fuel cell in order to predict overall trends with respect to undetermined parameters.

5 Fuel Cell Model Calibration

The objective in this section is to use experimental data to estimate the value of the four important adjustable parameters identified in the previous section. More precisely, the idea is to find the set of undetermined parameters values that provides the best match between numerical simulations results and experimental data.

Obtaining values for undetermined parameters of PEM fuel cell model has been done in recent literature. For example, Guo et al. [52] determined the model parameters including porosity, exchange current density and effective ionic conductivity of the electrolyte by least-squares fitting of experimental polarization curves measured at three different operating pressures. To seek the micro-structural parameters of the catalyst layer, Dobson et al. [53], coupled a multi-dimensional model of PEM fuel cell MEA with a nonlinear least-squares parameter estimation algorithm. The results revealed that only a unique set of structural parameters could accurately predict the multiple polarization curves measured over a range of operating conditions.

Hu et al. [54], adjusted two electrochemical parameters (i.e., $a_{j_0}^{ref}$ and $a_{j_0}^{ref} (353 K)$) while other geometric, operational and physical parameters where considered to be well determined or estimated. These two undetermined parameters were adjusted in such a way that the polarization curves obtained by numerical simulation were close to the experimental polarization curves obtained at various pressure and temperature. It is worth mentioning that the experimental data used in [54] were obtained from literature (i.e., by other research teams), and that some parameters values associated to the experimental fuel cell device had to be assumed. Utilization of experimental data that were measured by other groups and under conditions that do not specifically resemble the parameters used in those models were regularly found in literature [25, 55-57].
Similar to [52, 53], the strategy used in this section will allow determining the values of the four adjustable parameters by best-fitting polarizations curves obtained at various operating conditions, hence, the model will be considered to be valid over a range of temperature and pressure. Moreover, the experimental data used for the best-fitting step will have been generated by the authors of this text, hence, the operating conditions and all design parameters of the fuel cell are well determined and do not need to be guessed.

First, calibration of the model will be performed with the commercial/commercial fuel cell design (Figure 2(a)) in Section 5.1. Then, the parameters values obtained for the commercial electrodes will be used in Sections 5.2 and 5.3 for calibration of the remaining parameters for the home-made/commercial design (Figure 2(b)) and for the commercial/home-made design (Figure 2(c)), respectively.

### 5.1 Commercial/Commercial Fuel Cell Model Calibration

The fuel cell design made of commercial electrodes on both anode and cathode sides (see Figure 2(a)) is implemented in the numerical tools described in Section 3. The size of each layer of the 2D domain representing the fuel cell is given in Table 3. In the model, all parameters are well determined, except for the values of $a_{18}^{ref}$, $a_{18}^{ref}$ (353 K), $a_{c}$, and $a_{m}$.

In addition to the numerical simulation, an experimental measurement of the polarization curve for this fuel cell design was also performed as discussed in Section 2.3. First, measurements were obtained under an initial operating condition ($T_{fuel\ cell} = 80^\circ\text{C}$ and electrode backpressure = 15 psig), and the corresponding data are illustrated on a $V$-$I$ axis in Figure 5. Then, measurements were made at a different electrode backpressure (i.e., $T_{fuel\ cell} = 80^\circ\text{C}$ and electrode backpressure = 30 psig), and a different cell temperature (i.e., $T_{fuel\ cell} = 60^\circ\text{C}$ and electrode backpressure = 15 psig). The polarization curves corresponding to these different operating conditions are reported in Figure 5.

To perform the calibration process, a suitable variation range is selected for each of the four undetermined parameters (i.e., $a_{18}^{ref}$, $a_{18}^{ref}$ (353 K), $a_{c}$, and $a_{m}$). A finite group of values is selected within the range of each parameter. Then, different sets of model parameters are generated by considering all the possible permutations of the values of these four parameters (a total of 144 set of parameter values). Finally, the corresponding polarization curves are computed for each set of parameters values, for the three operating conditions described above. The polarization curves obtained by including each set of parameters in the numerical model are compared to the experimental data in order to find the parameter set that match the experimental data more closely. The best set of parameters is defined as the set that provides the minimal value of total error ($err_{tot}$), where $err_{tot}$ is defined as:

$$err_{tot} = \sum_{m=1}^{3} \left( \frac{\sum_{n=1}^{N} (i_{num,m}(V_n) - i_{exp,m}(V_n))^2}{N} \right)^2$$

In Eq. (8), the subscript $n$ is the identifier of the different electric potential values $V_n$ at which the numerical and experimental current density (i.e., $i_{num,m}(V_n)$ and $i_{exp,m}(V_n)$) are compared. Furthermore, the subscript $m$ identifies the operating conditions (pressure, temperature) at which the polarization curves were obtained (here, there are three operating conditions).
Hence, the error variable $err_{tot}$ represents the sum of squared differences between experimental and numerical current densities, considering all operating conditions tested.

The best set of parameters for the commercial/commercial fuel cell model was identified by selecting the curves that provide the minimal value of $err_{tot}$. That optimal set is reported in Table 5, and the polarization curves obtained by using these parameters values in the numerical tools are presented in Figure 5. More specifically, the three polarization curves obtained for the same three operating conditions through experimental measurements (i.e., $T_{\text{fuel cell}} = 80 \, ^\circ\text{C}$ and electrode backpressure = 15 psig, $T_{\text{fuel cell}} = 80 \, ^\circ\text{C}$ and electrode backpressure = 30 psig, and $T_{\text{fuel cell}} = 60 \, ^\circ\text{C}$ and electrode backpressure = 15 psig) are shown in Figure 5. First, it can be seen in Figure 5 that the impact of temperature and pressure are correctly represented by the model, i.e., the curves obtained by numerical simulations increases with the temperature, and increases with pressure. Moreover, the numerical curves follow correctly the trends of experimental curves with respect to temperature and pressure, i.e., they change with the good order of magnitude. This is possible due to the improvement of the model that were made in this work, i.e., by including Eqs. (3), (4) and (5), which capture the temperature and pressure dependence of several parameters.

It should be observed in Figure 5 that the model does not match perfectly the experimental data. However, the intent here is not to develop a highly accurate model. Actually, the intent is to develop a model that captures the general behaviour of the fuel cell with respect to various parameters.

To summarize, a set of parameters values that allows numerical simulation of fuel cell design using commercial electrodes (see Figure 2(a)) was identified. This set of parameters represents the electrochemical behaviour of the commercial electrodes. Hence, these parameters values will be used in the following sections, where commercial electrodes are included in the modified fuel cell designs.

5.2 Home-made/Commercial Fuel Cell Model Calibration

The fuel cell investigated in this section is operated under similar conditions to those applied to the fuel cell design made only with commercial electrodes (Section 5.1). Therefore, most of the parameters and governing equations are kept unchanged in the mathematical and numerical models. However, the geometrical parameters of the electrode on the anode side were modified according to the measured dimensions of the GDL (Toray carbon paper, TGP-H-060) and of the home-made electrode (see Figure 2 and Table 3). Moreover, the thermophysical properties of the GDL used for the home-made anodic electrode, such as porosity and permeability, are modified according to the available values from the technical data sheet of the suppliers.

The model associated to the fuel cell includes only one undetermined parameter, $a_{b,a}^{ref}$, which has to be found by best-fitting strategy. The other parameters ($a_{b,c}^{ref}$ (353 K), $\alpha_c$, and $\sigma_m$) are assigned the values reported in Table 5 (column “commercial/commercial”), because the same membrane (i.e., the same $\sigma_m$ value) and the same commercial electrode on the cathode side (i.e., the same $a_{b,c}^{ref}$ (353 K) and $\alpha_c$ values) are used in the current design.
Figure 6 presents the experimental data obtained by using the home-made electrode at the anode side, along with the best-fitted curves obtained from numerical simulations. The best-fitted numerical curves were obtained by identifying the value of \( a_{j0,a}^{ref} \) that minimizes the error defined in Eq. (8). The experimental and numerical polarization curves were obtained under three operating conditions, i.e.:

- (i) \( T_{\text{fuel cell}} = 80 \, ^\circ\text{C} \) and electrode backpressure = 15 psig,
- (ii) \( T_{\text{fuel cell}} = 80 \, ^\circ\text{C} \) and electrode backpressure = 30 psig, and
- (iii) \( T_{\text{fuel cell}} = 60 \, ^\circ\text{C} \) and electrode backpressure = 15 psig.

As can be noticed from this figure, there is some deviation between the numerical simulation results and the experimental data. The larger drop of voltage at higher current density observed for the experimental data in Figure 6 is typically associated to mass transfer limitations and flooding effects. However, the 2D, one-phase flow model used in this paper was not developed to capture such effects. Nonetheless, that simple model is clearly able to capture to trends of the polarization curve with respect to temperature and pressure.

The home-made and commercial anode can be compared by considering the \( a_{j0,a}^{ref} \) value. Typically, exchange current density based on the active surface area of the catalyst \( (\frac{i_{0,a}^{ref}}{A\,m^{-2}}) \) is used to evaluate the catalyst activity. However, the electrochemical surface area of the MOF derived electrocatalyst could not be estimated as no cyclic voltammetry measurements were available. Therefore, the term \( a_{j0,a}^{ref} \), that appears in Eq. (6) and is defined as a model parameter, is applied for catalyst evaluation.

Comparing the resulting \( a_{j0,a}^{ref} \) value for the home-made anode with the one obtained for commercial anodic electrode (see Table 5) reveals a one order of magnitude larger \( a_{j0,a}^{ref} \) in the case of the home-made anode. This can be attributed to either sufficient activity of MOF derived electrocatalyst for HOR or the effectiveness of the electrode structure. Considering the polarization curves measured with commercial and home-made anodic electrodes (Figures 5 and 6) it can be observed that while at low current densities the latter electrode provides slightly higher voltages, moving toward higher current densities, leads to an adverse trend and the former electrode reveals better performance (higher voltages at a given current density). Although at low current densities, the fuel cell performance is mainly limited by the kinetic of the oxidation, at medium current densities, proton (and oxygen) mass transport plays the dominant role. Therefore, it would be more reasonable to assume that performance deterioration results due to the incompetence of the home-made electrode’s structure. Interactions between Nafion ionomer and catalyst particles in the ink solution determine the structural properties of the electrode. Therefore, optimization of the Nafion ionomer content could provide a more effective home-made electrode and improve the fuel cell performance.

To summarize, by using the home-made electrode at the anode side only, it was possible to adjust the value of a single adjustable parameter \( a_{j0,a}^{ref} \) that characterizes the electrochemical behaviour of the home-made electrocatalyst. That value is reported in Table 5.

5.3 Commercial/Home-made Fuel Cell Model Calibration

The mathematical and numerical models are modified to take into account the size and the thermophysical properties of the GDL and the home-made cathode. The model associated to the fuel cell includes two adjustable parameters \( a_{j0,c}^{ref} (353 \, K) \) and \( \alpha_c \), which have to be found
by best-fitting strategy. Other parameters ($aj_{0,a}^{ref}$ and $\sigma_m$) are assigned to the values reported in Table 5 (column “commercial/commercial”), because the same membrane (i.e., the same $\sigma_m$ value) and the same commercial electrode at the anode side (i.e., the same $aj_{0,a}^{ref}$ value) are used in the current design.

Figure 7 presents the experimental curves obtained for the MOF derived electrocatalyst at the cathode side, along with the best-fitted curves obtained from numerical simulations. The best-fitted numerical curves were obtained by identifying the value of $aj_{0,c}^{ref}$ (353 K) and $\alpha_c$ that minimizes the error defined in Eq. (8). These values are reported in Table 5. The experimental and numerical polarization curves were obtained at three operating conditions. Again, there is some deviation between the numerical simulation results and the experimental data. Nonetheless, that model is able to capture to trends of the polarization curve with respect to temperature and pressure.

While $aj_{0,c}^{ref}$ (353 K) and $\alpha_c$ values obtained for the home-made cathode electrode were found equal to those attained with commercial electrode (Table 5), the overall performance of the MEA prepared from home-made cathode is lower than the one prepared from the commercial electrode (Figures 5 and 7). More specifically, considering the linear region of their polarization curves home-made electrode demonstrates higher ionic resistance than the commercial electrode. This also implies the insufficiency of the ink solution regarding its composition as increasing the Nafion ionomer content in the catalyst layer can reduce ohmic losses which occur due to proton transfer resistance.

To summarize Section 5, by using best-fitting strategy, it was possible to obtain the value of the adjustable parameters that characterize the electrochemical behaviour of the commercial and home-made electrodes, either on the anode or cathode side (see Table 5). By using these parameters, the model is able to capture the general trend of the fuel performance with respect to various parameters and operating conditions. In the following section, the values of adjustable parameters found in this section are included in the numerical model in order to identify optimization opportunities for the home-made electrocatalyst.

6 Predicted Impact of Nafion Content

Recent literature has shown that the performance of Pt-based electrodes can be improved by optimizing the content and distribution of Nafion in fuel cell catalyst layers. However, such studies have not yet been performed for the home-made electrodes fabricated from the MOF derived Pt-based electrocatalysts developed by the authors [6]. Hence, in this section, the numerical tools developed in the current work will be used to reveal if there are opportunities to improve the performance of home-made electrodes by optimizing their Nafion content. To do so, the parameters ($aj_{0,a}^{ref}$, $aj_{0,c}^{ref}$ (353 K), $\alpha_c$, and $\sigma_m$) calibrated in previous sections for commercial and home-made electrodes are included in the model.

6.1 Home-made/Commercial Fuel Cell Numerical Optimization
Parametric study of the current density is performed with respect to the Nafion content, \( \varepsilon_{m,\text{catalyst}} \), in the catalyst layer in order to determine its impact on the overall performance of PEM fuel cell using home-made electrodes at the anode side. It is worth mentioning that during this study, \( \varepsilon_{m,\text{catalyst}} \) was varied only at the electrode side in which home-made electrode is applied. The operating conditions used in the simulations are \( T_{\text{fuel cell}} = 80 \, ^\circ\text{C} \) and electrode backpressure = 15 psig.

Figure 8 exhibits the calculated current densities as a function of \( \varepsilon_{m,\text{catalyst}} \) for three different electric potentials (0.6, 0.4 and 0.2 V). As can be observed from this figure, according to the model, there is an optimal value of the Nafion content at each electric potential investigated. Moreover, the impact of the Nafion ionomer content on fuel cell performance looks very similar at three electric potential values investigated. In addition, the optimal value of Nafion ionomer is quite similar (average ~ 0.67) for the various electric potential investigated: it is 0.74 for 0.6 V, 0.68 for 0.4 V and 0.6 for 0.2 V. In other words, according to the numerical simulations the optimal Nafion content is robust, and should provide good fuel cell performance over a wide range of electric potential.

6.2 Commercial/Home-made Fuel Cell Numerical Optimization

A parametric study of the current density was also performed with respect to the Nafion content, \( \varepsilon_{m,\text{catalyst}} \), in the catalyst layer for the PEM fuel cell using home-made electrode on the cathode side. Again, \( \varepsilon_{m,\text{catalyst}} \) is varied only at the electrode side in which home-made electrode is applied. The operating conditions used in the simulations are \( T_{\text{fuel cell}} = 80 \, ^\circ\text{C} \) and electrode backpressure = 15 psig.

The impact of Nafion content on the calculated current densities is shown for three different electric potentials (0.6, 0.4 and 0.2 V) in Figure 9. It can be observed in this figure that there is again an optimal value of the Nafion content at each electric potential investigated. The optimal value of Nafion ionomer is also found to be robust (i.e., optimal value of 0.7 at 0.6 V, 0.7 at 0.4 V, and 0.6 at 0.2 V). This robustness is an important characteristic if the fuel cell is to be used in transient condition (various electrical potential values).

To verify the trend predicted by the model (i.e., the presence of optimal Nafion content values) for the home-made anode and cathode electrodes, experimental measurements were performed as reported in the next section.

7 Experimental Measurement of Nafion Content Impact

The two electrodes investigated numerically in Section 6 were fabricated and the PEM fuel cell polarization curves of the corresponding MEAs were experimentally measured for various values of Nafion content.

Catalyst ink solutions containing 10, 20, 25, 30, 35, 40 and 50 wt.% of Nafion were prepared. The weight percentage of Nafion ionomer in the catalyst layer is defined as:

\[
N(\text{wt}%) = \frac{w_{\text{Nafion}}}{w_{\text{Nafion}} + w_{\text{catalyst}}} \times 100 \quad (9)
\]
where, \( w_{Nafion} \) is the weight of dry ionomer and \( w_{catalyst} \) is the weight of MOF-derived catalyst. Hence, knowing the desired values of Nafion content \( N(\text{wt.\%}) \), it was possible to choose appropriate values for \( w_{Nafion} \) and \( w_{catalyst} \) during the ink preparation, by virtue of Eq. (9).

The volume fraction of the electrolyte phase in the catalyst layers \( (\varepsilon_{m,catalyst}) \) is related to Nafion content \( N(\text{wt.\%}) \) and can be calculated using the following expression [37]:

\[
\varepsilon_{m,catalyst} = \frac{N(\text{wt.\%}) \times (1/f) \times (m_{PL}/L_{eq})}{\rho_{N} \times (1 - N(\text{wt.\%}))}
\]  

(10)

where all the parameters have the same definition as before.

7.1 Home-made/Commercial Fuel Cell Experimental Measurement

First, the MEAs using home-made electrode at the anode side (illustrated in Figure 1 and 2(b)) were fabricated with the various Nafion content \( N(\text{wt.\%}) \) values listed above. These MEAs were included in the fuel cell test bench, one at a time, and the corresponding polarization curves are reported in Figure 10. In that figure, it can be seen that the Nafion content has an impact on the performance of the fuel cell (i.e., on the current density generated at a given voltage).

Furthermore, the values of the current density at three specific voltages were taken from this data and were reported in Figure 11. More specifically, Figure 11 depicts the current density with respect to the Nafion content for 0.6, 0.4 and 0.2 V. In these three cases, a maximum current density and an optimal value of Nafion content are clearly observed. The optimal value of Nafion volume fraction \( (\varepsilon_{m,catalyst}) \) is 0.04, corresponded to \( N(\text{wt.\%}) = 25 \text{ wt.\%} \), at 0.6 V, 0.4 V and 0.2 V, hence, the optimal values for that fuel cell design are similar for a wide range of electric potential. That robustness characteristic was also predicted by the numerical analysis.

It can be noticed that the optimal values of Nafion volume fraction at the three selected voltages from experimental measurements (~ 0.04) are not equal to those predicted by numerical simulation (~ 0.67). This is expected because the model neglects several transport phenomena. Nonetheless, the trends observed in Figure 11 are equivalent to those observed with the numerical analysis (Figure 8), i.e.,: (i) the presence of an optimal Nafion content, (ii) the optimal Nafion content is almost independent of the fuel cell voltage, and (iii) the dependency of the current density with respect to the Nafion content is similar at various voltage value.

7.2 Commercial/Home-made Fuel Cell Experimental Measurement

The MEAs using home-made electrode at the cathode side (illustrated in Figure 1 and 2(c)) were also fabricated with the various Nafion content values listed above. The corresponding polarization curves are reported in Figure 12. In that figure, it can be seen that the Nafion content at the cathode side has a larger impact on the performance of the fuel cell (i.e., on the current density generated at a given voltage), than on the anode side (Figure 10).

Values of the current density at 0.6, 0.4 and 0.2 V were taken from these data and reported in Figure 13. Again, several trends may be observed: there is an optimal Nafion content at all voltages; optimal values of Nafion volume fraction \( (\varepsilon_{m,catalyst}) \sim 0.06 \) corresponded to \( N(\text{wt.\%}) \)
= 35 wt.%, is almost independent of the fuel cell voltage, and (iii) the dependency of the current density with respect to the Nafion content is roughly similar at various voltage values. These trends were clearly predicted by the numerical model, even if the optimal values of Nafion volume fraction obtained experimentally (~ 0.06 from Figure 13) do not match those obtained numerically (~ 0.67 from Figure 9).

8 Discussion of the Results

As mentioned earlier, Nafion is needed in the catalyst layer to improve the contact between different phases and subsequently, increase the probability of electrochemical reaction occurrence. While low Nafion contents provide submissive protonic conductivity and lead to poor connection of the catalyst particles to the electrolyte solution, excess Nafion loading, prevents the efficient gas transfer to the catalytic active sites. At high current density region, the increase in water content causes even more resistance to gas transfer whilst promotes the flooding. The numerical and experimental results obtained in this study demonstrated the existence of an optimum Nafion ionomer content for anodic and cathodic home-made electrodes, however, this parameter was found to possess different values. Moreover, both numerical and experimental studies revealed that the impact of Nafion ionomer content on the fuel cell performance is more tangible at the cathode side. As mentioned before, the practical optimum values of Nafion content are different from the model estimations mainly due to the simplifications made during model development.

According to the numerical results, for the home-made anode operating at low overpotentials, after a certain point, increasing the Nafion content in the catalyst layer has a very small impact on the fuel cell performance (see Figure 8(a)). However, at larger overpotentials, the impact of Nafion content in catalyst layer \( \varepsilon_{m,\text{catalyst}} \) demonstrates a more considerable impact (Figure 8(b) and (c)). The numerical results demonstrated that unlike the anode side, for the home-made cathode, at all overpotential ranges Nafion ionomer content \( \varepsilon_{m,\text{catalyst}} \) affect the calculated current density values (see Figure 9). Moreover, at low and medium overpotentials, minimum computed value for current density is found for minimum electrolyte content. At high overpotentials however the minimum current density value calculated from the model corresponds to a maximum Nafion ionomer content. This indicates that too much ionomer in the catalyst layer can lead to significant mass transfer limitations especially at higher current densities and hence diminishes the fuel cell performance.

Based on the experimental results, varying Nafion ionomer content between 10 to 50 wt.% at the anode side results in a very small reduction in the fuel cell performance (Figure 10), while 25 wt.% Nafion content was found to be optimum. At the cathode side, Nafion ionomer content shows a larger impact on the overall performance of the PEM fuel cell compared to the anodic electrodes of different composition (Figure 12). Increasing the Nafion content from 10 % up to 35 wt.% in the cathode catalyst layer improves the fuel cell performance, however, further increment of Nafion causes performance reduction. This reduction can mostly be realized at high current density region. At this region, MEA containing 35 wt.% Nafion at the cathodic catalyst layer demonstrates the highest potential.
9 Conclusions

In spite of its well recognized impact on PEM fuel cell performance, previous studies did not reveal a uniform optimum value for Nafion ionomer content as it is found to be determined by various factors such as Pt loading in the Pt/C catalyst and type of electrocatalyst or carbon support. Therefore, it is essential to survey the effect of Nafion ionomer content in the catalyst layer of home-made electrodes fabricated from a MOF derived Pt-based electrocatalyst previously synthesized by the author’s research group [6].

The effect of model parameters on calculated fuel cell polarization curves was investigated via sensitivity analyses. Among the five undetermined model parameters: $a_{\alpha a}^{ref}, a_{\alpha c}^{ref}$ (353 K), $\alpha_\alpha, \alpha_c,$ and $\sigma_m$, only $\alpha_\alpha$ was found to be insignificant. This was in accordance with the results previously obtained with a more complex model [37] and confirms the adequacy of the model in predicting overall trends with respect to the parameters.

Excluding $\alpha_\alpha$, the four remaining adjustable parameters were estimated via model calibration using experimental data obtained for three different MEA designs investigated in the current study: i) commercial electrode at both anode and cathode sides, ii) home-made anodic and commercial cathodic electrodes and iii) commercial anode and home-made cathode electrodes.

Various operating conditions (two different cell temperatures and two different electrode backpressures) were considered to estimate undetermined model parameters by best-fitting several polarization curves obtained over a range of temperature and pressure.

The calibrated model was then used to survey the effect of Nafion ionomer content on the performance of home-made electrodes fabricated from a new MOF-derived Pt-based electrocatalyst at different electrical potentials (0.6, 0.4 and 0.2 V). The model predicted a robust optimal Nafion ionomer content for each of these potentials at which maximum current density was attained for home-made anodic and cathodic electrodes.

Finally, the qualitative trend predicted by the model regarding the optimal Nafion content was verified via experimental measurements. Electrodes containing a range of Nafion ionomer (10-50 wt.%) in their catalyst layers were fabricated and used in a single PEM fuel cell. According to the experimental measurements at the anode side 25 wt.% Nafion ionomer in the catalyst layer of home-made electrode resulted the best performing fuel cell, however, at the cathode side optimal Nafion content of 35 wt.% was observed. Although these optimal values were different from those obtained by numerical simulation, the model predicted trends with respect to the optimal Nafion content were similar to the experimental results. This discrepancy was related to several simplifications made during model development.

Therefore, in future works improvement of the current model to consider the three-dimensional transport phenomena, temperature gradient and two-phase flow will be attempted.

Acknowledgments
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List of Symbols

Variables

\( aJ_0^{ref} \) Exchange current density multiplied by specific surface area / A m\(^{-3}\)

\( C \) Molar concentration / mol m\(^{-3}\)

\( D \) Diffusivity / m\(^2\) s\(^{-1}\)

\( \text{error}_\text{tot} \) Total fitting error

\( f \) Mass percentage of platinum

\( F \) Faraday constant / C mol\(^{-1}\)

\( H \) Channel height / m

\( i \) Current density / A cm\(^{-2}\)

\( K \) Permeability / m\(^2\)

\( L_1 \) to \( L_{VII} \) Thickness of layers I to VII / m

\( m_{Pt} \) Platinum mass loading / mg cm\(^{-2}\)

\( N \) Nafion content / weight percentage

\( P \) Pressure / psig

\( r_\circ \) Electrochemical reaction rate / A m\(^{-3}\)

\( R \) Universal gas constant / J mol\(^{-1}\) K\(^{-1}\)

\( T \) Temperature / K

\( V \) Electrical potential / V

\( w \) Weight of catalyst or Nafion ionomer / mg

\( x \) and \( y \) Two gas species

Greek symbols

\( \alpha \) Transfer coefficient

\( \beta \) Kozeny-Carman constant

\( \varepsilon \) Porosity

\( \varepsilon_{m,catalyst} \) Nafion volume fraction

\( \rho_{Pt} \) Mass density of platinum / g cm\(^{-3}\)
\( \rho_c \) Mass density of carbon black / g cm\(^{-3} \)
\( \eta \) Overpotential / V
\( \zeta \) Stoichiometric ratio
\( \varphi \) Relative humidity
\( \sigma_m \) Electrolyte phase electrical conductivity / S m\(^{-1} \)

Subscripts

a Anode
c Cathode
CL In catalyst layer
exp Experimental
GDL In gas diffusion layer
H\(_2\) Hydrogen fuel
in Inlet
m Operating conditions identifier
n Electrical potential identifier
num Numerical
O\(_2\) Oxygen oxidant
OC Open circuit
out Outlet
Pt Platinum catalyst
porous In porous medium
s In solid phase

Superscripts
Ref Reference value

Abbreviations
GDL Gas diffusion layer
HOR Hydrogen oxidation reaction
MOF: Metal organic framework
MEA Membrane-electrode assembly
non-PGM Non-platinum group metal
ORR Oxygen reduction reaction
 PEMFCs Proton exchange membrane fuel cells

References

[40] COMSOL Multiphysics, COMSOL AB Inc.

Tables

Table 1 Operating conditions of the fuel cell

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Commercial (Home-made) electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{s,c}$</td>
<td>Operating parameter ∈ [1.15-0.5 / V]</td>
</tr>
<tr>
<td>$\zeta_a$</td>
<td>3</td>
</tr>
<tr>
<td>$\zeta_c$</td>
<td>3</td>
</tr>
<tr>
<td>$P_{a,\text{out}}$</td>
<td>15 / psig</td>
</tr>
<tr>
<td>$P_{c,\text{out}}$</td>
<td>15 / psig</td>
</tr>
<tr>
<td>$\varphi_{a,\text{in}}$</td>
<td>1</td>
</tr>
<tr>
<td>$\varphi_{c,\text{in}}$</td>
<td>1</td>
</tr>
<tr>
<td>$T$</td>
<td>80 °C</td>
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Table 2 Physical and electrochemical parameters with well-determined values used in the PEM fuel cell model

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_{GDL}$</td>
<td>0.3</td>
</tr>
<tr>
<td>$K_{GDL}$</td>
<td>$6.15 \times 10^{-12}$ / m$^2$</td>
</tr>
<tr>
<td>$e_{m,\text{catalyst}}$</td>
<td>0.05</td>
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<tr>
<td>$e_{CL}$</td>
<td>0.2</td>
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<tr>
<td>$C_{H_2}^{\text{ref}}$</td>
<td>40.88 / mol m$^{-3}$</td>
</tr>
<tr>
<td>$C_{O_2}^{\text{ref}}$</td>
<td>40.88 / mol m$^{-3}$</td>
</tr>
<tr>
<td>$D_{H_2,H_2O}^{\text{ref}}$(307 / K, 1 / atm)</td>
<td>$0.915 \times 10^{-4}$ / m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$D_{O_2,H_2O}^{\text{ref}}$(308 / K, 1 / atm)</td>
<td>$0.282 \times 10^{-4}$ / m$^2$ s$^{-1}$</td>
</tr>
</tbody>
</table>

Table 3 Geometrical parameters of the fuel cell

<table>
<thead>
<tr>
<th></th>
<th>Commercial anode/</th>
<th>Commercial anode/</th>
<th>Home-made anode/</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Commercial cathode</td>
<td>Home-made cathode</td>
<td>Commercial cathode</td>
</tr>
<tr>
<td>$H / m$</td>
<td>$126 \times 10^{-3}$</td>
<td>$126 \times 10^{-3}$</td>
<td>$126 \times 10^{-3}$</td>
</tr>
<tr>
<td>$L_1 / m$</td>
<td>$1 \times 10^{-3}$</td>
<td>$1 \times 10^{-3}$</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>$L_{II} / m$</td>
<td>$3.5 \times 10^{-4}$</td>
<td>$3.5 \times 10^{-4}$</td>
<td>$1.9 \times 10^{-4}$</td>
</tr>
<tr>
<td>$L_{III} / m$</td>
<td>$1.25 \times 10^{-4}$</td>
<td>$1.25 \times 10^{-4}$</td>
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</tr>
<tr>
<td>$L_{IV} / m$</td>
<td>$5.08 \times 10^{-5}$</td>
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<td>$L_V / m$</td>
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<td>$1.5 \times 10^{-4}$</td>
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</tr>
<tr>
<td>$L_{VI} / m$</td>
<td>$3.5 \times 10^{-4}$</td>
<td>$1.9 \times 10^{-4}$</td>
<td>$3.5 \times 10^{-4}$</td>
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<tr>
<td>$L_{VII} / m$</td>
<td>$1 \times 10^{-3}$</td>
<td>$1 \times 10^{-3}$</td>
<td>$1 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Table 4 Undetermined model parameters used in the sensitivity analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Base Value</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_j_0^{\text{ref}}$</td>
<td>$1 \times 10^9$ / A m$^{-3}$</td>
<td>$5 \times 10^{10}$-$5 \times 10^{11}$ / A m$^{-3}$</td>
</tr>
</tbody>
</table>
\( aj_{0,c}^{ref} (353 \, K) \), 2.5×10^{3} / A m^{-3} 1-1×10^{4} / A m^{-3} \\
\alpha_{a} \quad 1 \quad 0.25-1 \\
\alpha_{c} \quad 1 \quad 0.25-1 \\
\sigma_{m} \quad 14 / S m^{-1} \quad 6-14 / S m^{-1} \\

Table 5 Four series of adjusted parameters

<table>
<thead>
<tr>
<th></th>
<th>( aj_{0,a}^{ref} / A m^{-3} )</th>
<th>( aj_{0,c}^{ref} (353 , K) / A m^{-3} )</th>
<th>( \alpha_{c} )</th>
<th>( \sigma_{m} / S m^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial electrodes</td>
<td>5×10^{8}</td>
<td>5×10^{3}</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Home-made anode</td>
<td>5×10^{9}</td>
<td>5×10^{3}</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>Home-made cathode</td>
<td>5×10^{8}</td>
<td>5×10^{3}</td>
<td>1</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure Captions

Fig. 1  Schematic representation of the fuel cell device: (a) three dimensional exploded view, (b) channels pathways, and (c) two dimensional cross section of MEA and bipolar plates.

Fig. 2  Illustration of the three fuel cell design: (a) commercial electrodes on both anode and cathode sides, (b) home-made electrode on the anode side, and (c) home-made electrode on the cathode side.

Fig. 3  Two dimensional (along the channel) domain of the mathematical and numerical model.

Fig. 4  Polarization curves generated by numerical simulation. (a) impact of \( aj_{0,a}^{ref} \), (b) impact of \( aj_{0,c}^{ref} (353 \, K) \), (c) impact of \( \alpha_{a} \), (d) impact of \( \alpha_{c} \), and (e) impact of \( \sigma_{m} \).

Fig. 5  Polarization curves obtained from numerical simulations (solid lines) and experimental results, for the fuel cell design using commercial electrodes.

Fig. 6  Polarization curves obtained from numerical simulations (solid lines) and experimental results, for the fuel cell design using the home-made electrode on the anode side.

Fig. 7  Polarization curves obtained from numerical simulations (solid lines) and experimental results, for the fuel cell design using the home-made electrode on the cathode side.

Fig. 8  Numerical prediction of the impact of Nafion content on the current density, for the fuel cell design using home-made electrode on the anode side for electrical potential of (a) 0.6, (b) 0.4 and (c) 0.2 V.
Fig. 9  Numerical prediction of the impact of Nafion content on the current density, for the fuel cell design using home-made electrode on the cathode side for electrical potential of (a) 0.6, (b) 0.4 and (c) 0.2 V.

Fig. 10  Measured polarization curves of the fuel cell design using home-made electrode on the anode side, for various Nafion content.

Fig. 11 Measurement of the impact of Nafion content on the current density, for the fuel cell design using home-made electrode on the anode side for electrical potential of (a) 0.6, (b) 0.4 and (c) 0.2 V.

Fig. 12 Measured polarization curves of the fuel cell design using home-made electrode on the cathode side, for various Nafion content.

Fig. 13 Measurement of the impact of Nafion content on the current density, for the fuel cell design using home-made electrode on the cathode side for electrical potential of (a) 0.6, (b) 0.4 and (c) 0.2 V.
Fig. 1
Fig. 2
Fig. 3
Fig. 5
Fig. 6
Fig. 7
Fig. 8
Fig. 10
Fig. 11
Fig. 13