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Three dimensional model of a high temperature PEMFC using PBI doped phosphoric acid membranes. Study of the flow field effect on performance

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Abstract

A three-dimensional isothermal model of a high temperature polymer membrane fuel cell equipped with polybenzimidazole (PBI) membrane is described. All major transport phenomena were taken into account except the species cross-over thought the membrane. The cathode catalyst layer was treated as spherical catalyst agglomerates with porous inter-agglomerate spaces. The inter-agglomerate spaces were filled with a mixture of electrolyte (hot phosphoric acid) and polytetrafluoroethylene (PTFE). This approach proved to be an essential requirement for accurate simulation. In this particular paper the influence of different flow field designs and dimensions on performance was intensely study. Traditional configurations were tested (straight, serpentine, pin-in and interdigitated), and a new designs were proposed. With these new designs we tried to maximize performance by providing homogeneous reactants distribution over the active area keeping low pressure drop and relatively high velocity. The dimension and position of the inlet and outlet manifolds were also analysed. From the obtained results was observed a massive influence of the manifolds position and dimension on performance. This fact leaded to an optimization of the manifolds which can give important guidelines for future bipolar plates production.

Keywords: *Modelling; PEMFC; Polybenzimidazole; Flow Field; High Temperature*

1 Introduction

During the last decade fuel cell modelling became an extremely important toll for design and understanding of all chemical and physical phenomena related with this technology. With the increase of computer power, three dimension (3D) modelling became a reality; which opened the door to complex modelling procedures using computational fluid dynamics (CFD).

In terms of high temperature polymer electrolyte membrane fuel cells (HT-PEMFC) little work has been published until 2010. In 2006 Cheddie and Munroe [1] produced a 3D model where they compared 3D results with the previous 2D model. They found that the 2D model overestimated performance by neglecting rib effects. The oxygen depletion occurred mainly in the catalyst layer under the ribs, and it was more predominant at lower flow rates. They also analysed the temperature profile inside the cell, the hottest point was observed in the membrane under the land and a temperature variation in the cell of 19 K was observed.

In the same year, Peng and Lee [2] developed a 3D non-isothermal model which used as computational domain a single straight channel. Like Cheddie and Munroe [1] they also found that the maximum current densities occurred under the land areas. With the analysis of the temperature profile they found that the higher temperature was located in the cathode catalyst layer and the temperature variation across the cell increased with increasing current density. In 2008 Peng et al. [3] used the same computational domain of the previous work to develop a 3D dynamic model. Its main feature was the introduction of the layer charge/discharge effect. In 2009, Ubong et al. [4] developed a simple 3D model for a single cell with triple serpentine flow channels equipped with a PBI membrane fabricated by BASF Co., USA. The computational domain included a section of the PBI membrane and both cathode and anode gas flow channels, GDLs and catalyst layers. They used this model to predict performance and polarization curves. More recently, Lobato et al. [5] developed a CFD model for a 50 cm^2 half-cell. The model was solved for three different flow channel geometries (4-step

serpentine, parallel and pin-type). They found that the parallel flow channels presented a significant lower performance probably due to preferential paths, which makes the reactants gases not to be well distributed.

In this paper a 3D isothermal and steady state model for an experimental HT-PEMFC is presented. The model developed for the 3D simulations was based on previous works published by the authors [6-9]. In this study, the main objective was the investigation of the effect of different flow field designs on performance. Topologies of the gas flow fields can normally include pin, straight, serpentine, or interdigitated. These designs should be optimised in order to provide a uniform distribution of the reactants gases over the respective active electrode surface to minimize the concentration over-potential.

2 Fuel Cell Model

2.1 Computational Domain and Assumptions

Details of all methods and materials used in the experimental tests as well as the physical characteristics of the fuel cell can be find in [10]. The computational domain for the base case (geometry and conditions similar to the experimental cell) is shown in Fig. 1. Basically, it consisted in 12 straight channels on both sides of the membrane electrode assembly (MEA). The MEA had 5 layers: anode gas diffusion layer (GDL), anode catalyst layer, PBI membrane, cathode catalyst layer and cathode GDL.

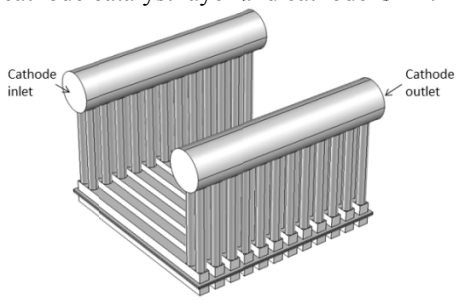

Fig. 1. Computational domain of the base case.

In this model several assumptions (which are shared with almost all HT-PEMFC models) were adopted to facilitate the calculations:

- Steady state operation
- Isothermal operation
- Single phase flow
- Ideal gas mixtures
- Porous media was assumed to be isotropic and macro- homogeneous.
- The PBI membrane was assumed to be impermeable to gas flow.
- Negligible contact resistance between components.

Other simplifications regarding the governing equations were done but they will be introduced later on, as the equations are presented.

2.2 Governing Equations

Physical phenomena occurring within the fuel cell under isothermal operation are described by the solution of conservation equations for mass, momentum, species, and charge transport. In this section a brief summary of the equations used by the model are presented.

In order to simply the calculations it was assumed constant viscosity and density for gas mixture. This fact led to the following equations for the conservation of mass and momentum.

$$\nabla \cdot \mathbf{v} = 0 \qquad (1)$$

Where, $\mathbf{v}$ is the velocity vector. Using equation 1(equation of continuity) the conservation of momentum could be simplified to give:

$$-\nabla p + \mu \nabla^2 \mathbf{v} + \rho \mathbf{g} = S_1 \qquad (2)$$

Where, p is the pressure, μ is the viscosity, ρ is the density, $\mathbf{g}$ is the gravity vector, and S_1 is the source term. The solution of equation 2 gives the velocity and pressure field. When the source term is zero, i.e. in the channels, equation 2 becomes the celebrated Navier-Stokes equation. To account the force exerted by the fluid on the porous matrix the source term in the porous regions became:

$$S_1 = -\frac{\mu}{K}(\epsilon \mathbf{v}) \qquad (3)$$

Where, K is the permeability, and ε is the porosity.

The conservation of species was described by the Stefen-Maxwell equations for the transport of multi-component gas species:

$$-\rho \mathbf{v} \cdot \nabla w_i - \nabla \cdot \left[-\rho \sum_{j=1}^{n} \tilde{D}_{ij} \left(\nabla x_j + \left(x_j - w_j \right) \frac{\nabla p}{p} \right) \right] = r_i \qquad (4)$$

Where, w_i is the mass fraction of the species i, x_j is the mole fraction of the species j, $\tilde{D}_{ij}$ is the multi-component Fick diffusion, r_i is the source or sink term of the species i. The solution of equation 4 gives the mass fraction of the different gas species in the mixture. r_i is zero everywhere except in the catalyst layers where the reaction takes place.

$$r_{H_2} = \frac{j_a}{2F} M_{H_2} \qquad (5)$$

$$r_{O_2} = -\frac{j_c}{4F} M_{O_2} \qquad (6)$$

$$r_{H_2O} = \frac{j_c}{2F} M_{H_2O} \qquad (7)$$

Where, M is the molecular mass of each species, F is the Faraday constant, j_a is the anode volumetric current density, and j_c is the cathode current volumetric current density. The volumetric current densities will be described afterwards.

The equations for the conservation of charge were obtained thorough Ohm's law and the relationship between the electric field and the potential gradient.

$$\nabla \cdot (-\sigma \nabla \varphi) = S_2 \qquad (8)$$

Where, σ is the electric or protonic conductivity, φ is the electric or protonic potential and S_2 is the source term. The source term accounts for the generation and consumption of protons and electrons. Therefore, it was zero everywhere except in the catalyst layers, in these regions was equal to the volumetric current density.

The catalyst layers were treaded as spherical agglomerates of catalyst particles with a porous inter-agglomerate space, where each agglomerates was covered by a thin film of phosphoric acid.

To describe the electrochemical kinetics in these conditions a modified version of the Butler-Volmer equation was used.

$$j = nFC_{g/l}\left[\frac{1}{E_r k(1-\varepsilon)} + \frac{(r_{agg}+\delta)\delta}{r_{agg}a_{agg}D_{liq}}\right]^{-1} \quad (9)$$

Where, n is the number of changed electrons, $C_{g/l}$ is the concentration of the reactants at the gas/liquid interface, E_r is the effectiveness factor, a_{agg} is the agglomerate effective surface area, r_{agg} is the agglomerate radius, D_{liq} is the reactants diffusion in phosphoric acid, δ is the thin film thickness, and k is the reaction rate given by the next equation.

$$k = \frac{i_0}{nF(1-\varepsilon)C_{l/s}}\left[\exp\left(\frac{-\alpha_{Rd}F}{RT}\eta\right) - \exp\left(\frac{\alpha_{Ox}F}{RT}\eta\right)\right] \quad (10)$$

Where, i_0 is the exchange current density corrected for the particular conditions of pressure and temperature, $C_{l/s}$ is the reactants concentration at the agglomerate surface, α is the transfer coefficient (oxidation or reduction evolution), T is the temperature, R is universal gas constant, and η is the overpotential.

For a complete description of the governing equations and system parameters references [6-8] should be consulted.

2.3 Boundary conditions

To solve the governing equations is necessary to employ boundary conditions for each conservation equation. Therefore, for the conservation of momentum, volumetric flow rate was set at the inlets (in the anode side 2.5 x 10^{-6} m^3 $s^{-1}$and at the cathode side 7.5 x 10^{-6} m^3 s^{-1}) and pressure at the outlets (atmospheric pressure). For the conservation of species the mass fraction of the different species was set at the inlets and at the outlets convective flux was assumed. The solid phase potential was prescribed at the land/GDL interface. For the anode side it was set to zero volts, and to the cell potential at the cathode side. For the electrolyte phase the potential was only required to prescribe electrical insulation to the exterior boundaries formed by the membrane and catalyst layers.

2.4 Solution methodology

To solve the governing equations COMSOL Multiphysics version 4.2 was used. The computations were performed on a 64 bit Windows platform with 16 GB of RAM, and Intel Core i7-2600 CPU 3.4 GHz processor. To solve this model a parametric segregated solver which allowed splitting the solution into sub-steps was used. With this technique both memory and assembly time could be saved, which was critical due to the very high number of degrees of freedom.

3 Results

With this work we tried to understand the effect of different flow field configurations on performance. Therefore, different computational domains were created. All classic configurations (straight, pin, serpentine and interdigitated) were tested and performance compared with each other. In addition, the manifolds dimensions were also analysed.

As mentioned before, this 3D model was based on previous 2D models created by the authors. All these models were subject to an intensive validation procedure [8] and therefore it was assumed that the 3D model had the some behaviour of the previous models. Figure 2 shows a comparison between experimental and data obtained at 150 °C and 1atm and simulation results.

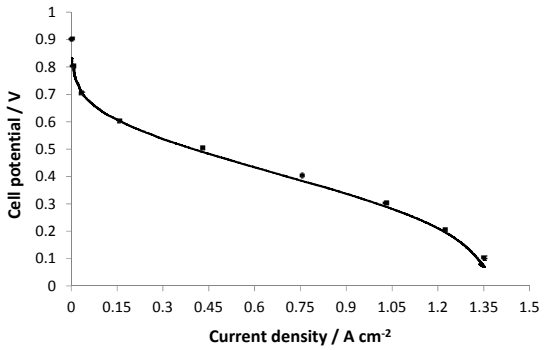

Fig. 2. Comparison between modelled and experimental data. — experimental data; • model results.

As is possible to see experimental and simulation results were in good agreement. Previous 2D models were tested at different operation conditions and the results also shown a good fit with the experimental data [8].

3.1 Performance

The impact of the flow fields on performance was analyzed through the observation of the predicted polarization curves. It is important to note that exactly the same parameters were used in all designs; therefore, all differences on performance were only related to geometric issues.

The interdigitated design showed, by far, the best performance. These results proved how performance can be improved if the transport of species through the porous media is made by means of convection and diffusion. With this geometry the

gas flow is forced to pass through the porous media to reach the outlet, as a consequence of this, species molecules can reach the catalyst surface much faster. In the other designs the gas flow is not forced to go through the porous media; therefore, the gas species only reach the catalyst surface by means of diffusion. The results for the straight, pin and serpentine designs were very similar except at very low potentials. In this region the mass transport effect became very significant; therefore, the design that better distributed the reactants showed the best results, in this case was the pin flow field. Fig. 4 shows the current density distribution at the cathode catalyst layer/GDL interface at 0.2 V. From this figure is possible to see how the geometry influenced the distribution of current density.

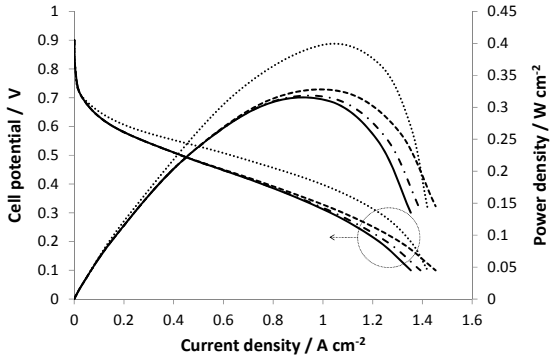

Fig. 3. Comparison between modelled data when four different flow field designs were used. — straight data; – • – serpentine; – – pin; ••• interdigitated.

In all flow field designs the maximum current density was obtained in the regions under the channels near the inlet, due to very high oxygen concentration in this region. As the gas flow approached the outlets the current density decreased gradually, cause by oxygen depletion. From the analyses of Fig. 4 the pin flow field seemed the best option to use as a flow field, because the current density was better distributed over the active area. With the interdigitated flow field the power output is the highest, however, the current density was not distributed evenly. This fact could lead to hot points in the MEA and thermal stresses.

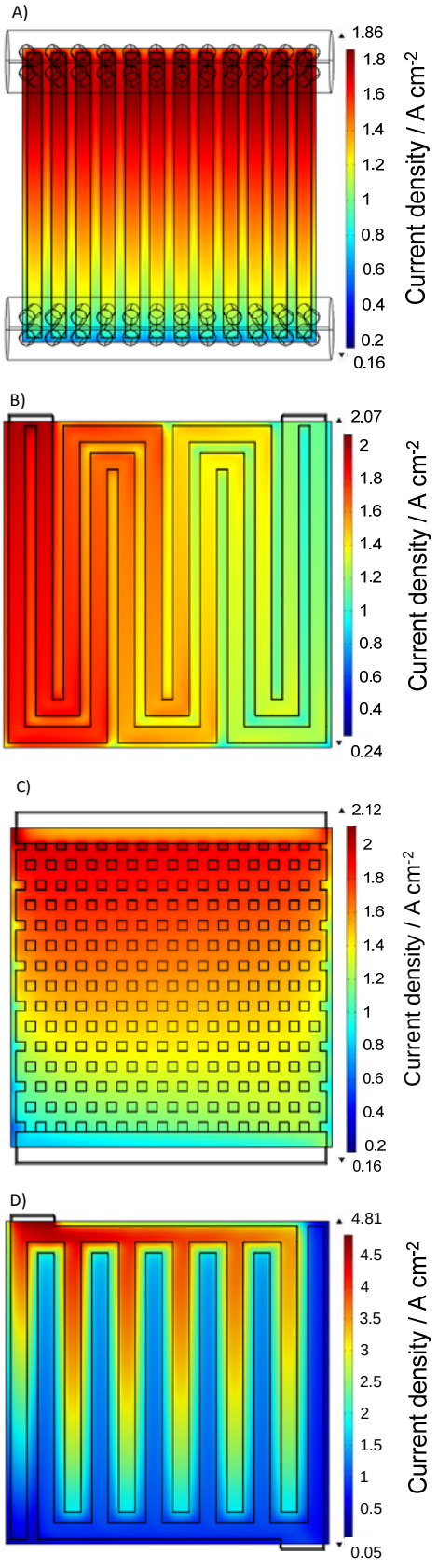

Fig. 4. Current density distribution at the cathode catalyst layer/GDL interface at 0.3 V. A) Straight; B) Serpentine; C) Pin; D) Interdigitated.

3.2 Manifolds Effect

The manifolds dimensions and the position of the gas inlets and outlets are extremely important for the general cell performance. To study the effect of these features several tests were done.
To demonstrate how preferential flow paths affect performance two simulations with straight flow channels were done. In the first one the manifolds had a cross section area of 2.25mm^2, and in the second one the cross section area was the double (4.5 mm^2). The current density counter maps and the velocity arrows can be visualized in Fig. 5.

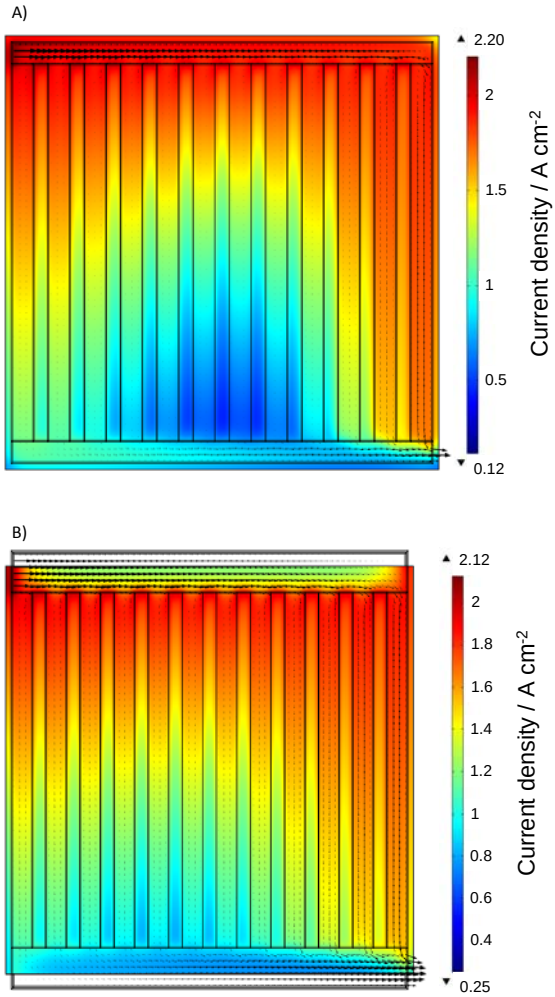

Fig. 5. Current density distribution at the cathode catalyst layer/GDL interface at 0.3 V. A) Manifold cross section area 2.25 mm^2; B) Manifold cross section area 4.5 mm2.

Fig. 5 shows clearly (through the velocity arrows) how the flow followed preferential paths when manifolds with small cross area were used. This fact can be related with the higher inlet velocity inherent to this topology. As a result of this phenomenon, the current density distribution was not even through the active area at low potentials; as expected, was much higher near the channels with higher flow rate. This problem could be solved by increasing the cross section area of the manifolds. In this case, the current density distribution was improved, which meant an increase of in 0.12 A cm^2 the limiting current density (Fig. 6).

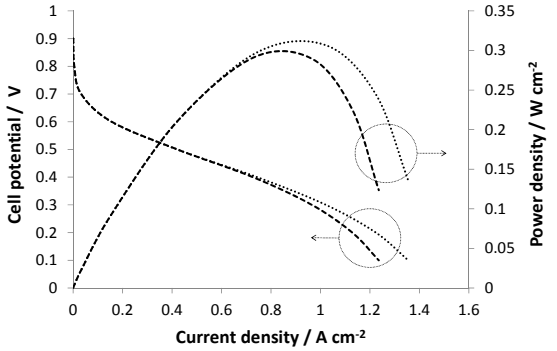

Fig. 6. Comparison between modelled data when two different manifolds were used. – – Manifold cross area 2.25 mm2; ••• Manifold cross area 4.5 mm2.

The current density distribution could be forward improved by changing the position of the inlet and outlet manifolds.

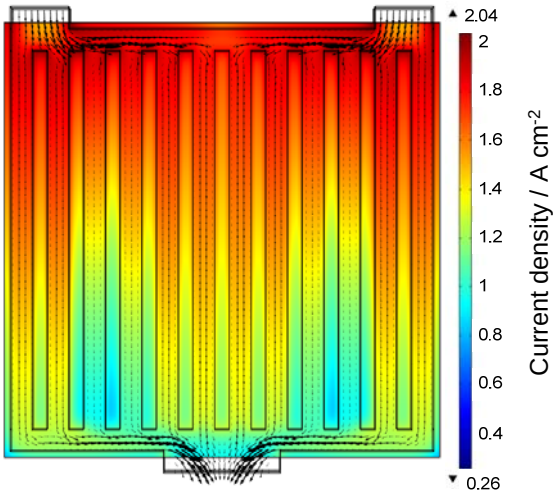

Fig. 7. Current density distribution at the cathode catalyst layer/GDL interface at 0.3 V.

Fig. 7 shows one of the studied cases where this possibility was analysed. With this new configuration the entire active area was used efficiently. A significant improvement can be seen when figures 5 and 7 are compered. In Fig 7. the dark blue regions (very low current densities) almost disappeared, this fact indicates a good distribution of the reactants on the active area. Ideally, all gas channels should have the same mass flux. Figure 8 shows the O_2 mass flux in the middle

of flow field at 0.3V for the 3 topologies. As is possible to see the last analysed geometry had the most uniform distribution with a standard deviation of 0.034. On the other hand, the first geometry (manifolds cross section area of 2.25 mm^2) had the worst distribution with a standard deviation of 0.082.

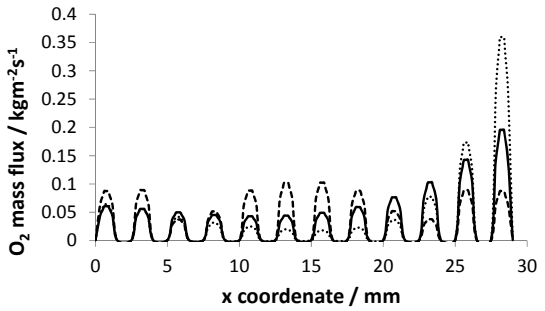

Fig. 8. O2 mass flux profile in the middle of flow field at 0.3 V. — new geometry; – – Manifold cross section area 4.5 mm^2; ••• Manifold cross section area 2.25 mm^2.

4 Conclusion

From the obtained results several conclusions could be drawn. It was proven that interdigitated flow field topology delivered the highest power output. However, it does not represent a suitable solution to this fuel cell system because hot points could be generated due to heterogeneous current density distribution. Besides, the phosphoric acid in the catalyst layer could be washed out with the gas convective flow. Therefore, pin topology proved to be the ideal flow field geometry.
The manifolds dimensions and position had a massive influence on performance. Consequently, this aspect should be subject of massive study for optimization proposes. In this study a new geometry was suggested in order to homogenize the mass flux in the straight channels geometry.

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