

Numerical Study of Microfluidic Fuel Cell Performance

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Abstract: Using COMSOL Multiphysics 3.5, a numerical model has been developed to determine the effect of the channel geometry and electrode configuration on cell performance based on polarization curves. The Butler-Volmer equation was implemented to determine the reaction rates at the electrodes. The Conductive Media DC module is used to model the electric fields within the fuel cell. The concentration distributions of the reactant species are obtained using the Incompressible Navier-Stokes and Convection and Diffusion modules. Solving these equations together predicts the current density for given cell voltage values. The results demonstrate the cell voltage losses due to activation, ohmic and concentration overpotentials. COMSOL Multiphysics was used to test different channel aspect ratios and electrode configurations that led to reduced overpotentials without conducting lengthy and expensive experiments.

Keywords: Microfluidic fuel cell, Numerical modeling, COMSOL Multiphysics, Polarization curve

1. Introduction

Recently, there has been a growing demand for a small but high power source of energy for portable devices which are expected to function for long period of time without the need for recharging [1]. The current battery technology can hardly keep up with this growing power demand [2]. A recent comparison between Li-ion batteries and fuel cells has shown that the latter has much higher power density and hence more potential to respond to the future supply and demand [2]. Since the reactions in fuel cells are surface based, miniaturization of fuel cells, which increases the surface-to-volume ratio, leads to the further improvement of the power density that is required for portable devices [3, 4]. Thus, miniaturized fuel cells are capable of bridging the gap between the battery technology and the high power density required for the portable applications. A prodigious amount of research has been conducted on the

miniaturization of the conventional fuel cells [5-7]. Although the energy density of the miniaturized fuel cells increases as their size continues to shrink, several technological and mechanical challenges (including efficiency issues related to water and heat management, the ohmic overpotential caused by the membrane, and machining of the graphite bipolar plates) still remain [6, 8]. These challenges limit the further decrease in the size and hence limit the increase in the power density of miniaturized fuel cells.

Recently, a novel design and structure of the fuel cell, called the microfluidic fuel cell, has been introduced to overcome the above limitations of miniaturized fuel cells. In such systems, the fuel and oxidant are introduced in a microchannel through separate inlets and form a co-laminar flow between the electrodes which are typically positioned along the channel. Laminar flow maintains separation of the fuel and oxidant. This eliminates the need for the membrane and overcomes the membrane-related issues such as the ohmic overpotential and water management. Due to the laminar nature of flow in these systems, the transport phenomenon is diffusion limited and hence the channel geometry plays an important role. Bazylak et al. [1] tested three different channel cross sections with different aspect ratios, obtained the fuel and oxidant distribution, and calculated the fuel utilization. They found that the rectangular cross sections have higher fuel utilization compared to the square one. Chang et al. [9] also conducted a numerical analysis for a fixed flow rate and fixed channel cross section aspect ratio (i.e., height to width ratio). They reported that a reduction of cross-sectional area results in higher fuel cell performance. They also observed that for a constant cross sectional area, the high aspect ratio results in higher cell performance.

In previous studies, the current and power densities were conventionally normalized by the electrode surface area. However, it is reasonable to normalize the current and power densities by the overall fuel cell volume, as it is critical in developing compact power sources for portable devices.

Since the species transportation to the active sites is only by diffusion, the channel geometry plays an important role in the overall performance of the system. In this paper, three different channel geometries (Fig. 1) have been modeled and tested by COMSOL Multiphysics to find out the geometry with highest performance. Cell polarization curves are used as a quantitative measure for performance.

2. Geometry

One important geometrical factor affecting the performance of a microfluidic fuel cell is the aspect ratio, defined as the ratio of the channel height to the channel width. To examine the effect of changing the relative height and width, micro-channels with square and high and low aspect ratio rectangular cross-sections are examined numerically. The channels were designed such that the cross-sectional area was consistent for all the cases (i.e., square cross sectional area and high and low aspect ratio rectangular cross-sections). The channel length and length of the inlets was also the same for all the cases. A typical Y-shaped microchannel was considered. Figure 1 presents the schematic of the channel and cross sections for each aspect ratio with relevant dimensions. Since the fluid flow patterns, reactant distributions, and electric fields are symmetrical about a plane bisecting the height of the channel, only the upper (or lower) half of the channel was modeled in order to use finer meshes with reduced memory requirements.

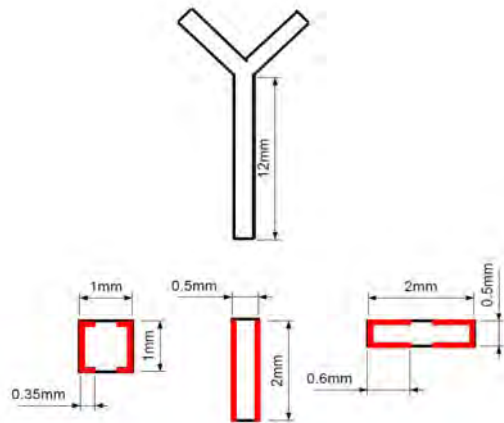


Figure 1. The schematic and dimensions of the channel and cross-sections presented here. The electrode surfaces are indicated by the bold red lines.

Designing electrodes for a microfluidic fuel cell is a task which requires attention: generally it is desirable to maximize the active area to maximize the use of the reactants and increase the output current of the cell. However, the electrodes must be placed so that they are only in contact with one reactant species as cross-over of either fuel or oxidant to the opposite electrode will hamper performance [1]. In microfluidic fuel cell operation, fuel and oxidant species are able to diffuse across the co-laminar interface and form a mixing region which grows in width along the channel. The mixing region is hourglass shaped, being wider near the top and bottom of the channel where the flow velocity is lower. The mixing region should not overlap with either electrode. This limits the available area on the channel walls where electrodes can be placed.

To determine the maximum allowable extent of the electrodes across the width of the channel, the concentration distributions were calculated for each channel design by solving the fluid flow and mass-transport equations with no reaction on the boundaries. The maximum width of the mixing region is determined from a plot of concentration distributions on the upper edge of the channel outlet. Once this width is determined, the electrode subdomains are added on the side walls of the channel and extending across the top and bottom of the channel up to the extent of the mixing region. Of course, since only half of the channel was modeled in this analysis, electrodes were only added to either the upper or lower surface but not both. This electrode design procedure allows for maximum electrode area while avoiding reactant cross-over. In this study, no electrode boundaries were added on the top and bottom of the high aspect ratio channel since these electrodes would not add any appreciable active area. The electrodes of the square cross section were extended up to the maximum possible width (without overlapping with the mixing region), but electrodes of the low-aspect ratio were extended just enough to create the same active area as in the square channel in order to make a better comparison between the performances of the two cells.

Typically, the electrodes of a microfluidic fuel cell are formed by sputtering, electroplating, or otherwise adhering a platinum catalyst to a highly conductive metal current collector on the

channel walls [10]. This process results in impermeable electrodes and makes the reactions surface-based. It is therefore important to maximize the active area within the channel. One way to model the electrochemical reactions on these electrodes would be to consider current and reactant species flux boundary conditions on the channel walls where the electrodes are located. However, our preliminary results showed that these kind of boundary conditions result in an unstable model. Thus, the electrodes were implemented as thin (25 μm) subdomains, within the main channel. The flow of electrolyte was assumed to continue within these subdomains, but species and current source terms were added for the potential and convection-diffusion equations (see Governing Equations below).

3. Governing Equations

In order to predict the effect of activation, ohmic, and concentration overpotentials on fuel cell performance, a set of steady-state conservation equations is used to model fuel cell operation. The values of the various parameters used in the model are given in the Appendix.

3.1 Fluid Flow

Microfluidic flows are characterized by low Reynolds numbers due to the small dimensions of microchannels and low fluid velocities. For this reason, the flow is expected to be laminar and can be assumed to be incompressible. Also, in a typical micro-scale flow, the volume forces such as the fluid weight are dominated by surface forces such as viscous shear stress. Applying mass and momentum conservation in differential form allows the velocity field to be described by the Navier-Stokes and continuity equations [11].

$$\begin{aligned}\nabla \cdot \mathbf{v} &= 0 \\ \rho(\mathbf{v} \cdot \nabla \mathbf{v}) &= -\nabla p + \mu \nabla^2 \mathbf{v}\end{aligned}$$

In these equations, \mathbf{v} and p are the velocity and pressure, respectively. These equations can be implemented using the steady-state, laminar incompressible flow module of COMSOL Multiphysics. The flow was assumed to continue into the electrode subdomains. The no-slip boundary condition was applied to all of the

channel walls. At the symmetry plane defining the top or bottom of the model geometry, a symmetry boundary was applied. A constant velocity was applied to the inlets, and the outlet was assumed to discharge to atmospheric pressure.

3.2 Charge Conservation

Since both the fuel and oxidant are dissolved in acidic electrolyte, the concentration of hydrogen ions was assumed to be uniform throughout the channel. Transport of protons from the anode to the cathode is by electric migration only. In these circumstances the transport of charged species and the electric field within the electrolyte can be modeled using the potential equation from the Conductive Media DC module:

$$\sigma \nabla \cdot \nabla \phi_e = 0$$

where, ϕ_e is the local potential in the electrolyte. Electric insulation boundary conditions were applied to all of the channel surfaces. Within the electrodes, where charged species are generated or consumed, a current source is applied and the local current density is calculated by the Butler-Volmer reaction kinetics equation (see Reaction Kinetics).

A second Conductive Media DC module was used to describe the voltage and current distributions within the solid phase metallic electrodes.

$$\sigma \nabla \cdot \nabla \phi_s = 0$$

Because the metallic electrodes and current collectors are highly conductive, a large value for conductivity (10^7 S/m) was used for this module. Applying a potential boundary condition for the outer electrode walls resulted in an essentially uniform solid phase voltage, ϕ_s over the entire subdomain. The other boundaries were assigned electric insulation boundary conditions.

3.3 Mass Transport

Once the velocity field within the microchannel has been determined by the Navier-Stokes equation, it is possible to use the

calculated velocity to model the mass transport phenomena. In microfluidic fuel cells, the reactant species are transported along the length of the channel by convection. However, diffusive transport in a direction transverse to the flow is necessary to replace reactant species in the vicinity of the electrodes, as they are consumed by the reaction. When concentrations are sufficiently low, interactions between different solute species can be ignored and diffusion rates can be assumed to be linearly proportional to concentration gradients [1]. In this model, the system is assumed to be isothermal, and pressure differences are not large enough to influence diffusion coefficients. Implementing these assumptions allows the concentration distributions of the fuel and oxidant to be described by Fick's law given as

$$\nabla \cdot (-D\nabla c + c\mathbf{v}) = 0$$

where, c is the local concentration of the reactants. At the inlets, a uniform concentration is applied. At the outlet, convective flux dominates mass transport and the concentration gradient normal to the outlet is set to zero. Since no transport is possible through the channel walls, all of the channel walls are assigned insulation boundary conditions. Within the electrode subdomains, a source term is added (see Reaction Kinetics).

3.4 Reaction Kinetics

The Butler-Volmer reaction kinetics equation describes the local current density, i , across the electrode surface which is related to both the applied electric potential and the concentration of reactant species [9].

$$i = i_0 \frac{c}{c_{REF}} \left[e^{\left(\frac{\alpha n F}{RT} \eta\right)} - e^{\left(\frac{-(1-\alpha) n F}{RT} \eta\right)} \right]$$

In this equation, η is the activation overpotential. The reactant species are consumed at a rate, S , which is proportional to the current density [9].

$$S = \frac{i}{nF}$$

At each electrode, it is necessary to calculate the activation overpotential which is required to overcome irreversibilities as the reaction deviates from its equilibrium state.

$$\eta = \phi_s - \phi_e - E_{REVERSIBLE}$$

The potentials of the solid electrode, ϕ_s , and the adjacent electrolyte, ϕ_e , are found by solution of the potential equations. The reversible potential was taken as a constant value which is based on the reaction Gibbs free energy change at standard conditions. Although the reversible potential varies with the local concentrations of reactants and products in the electrolyte, the concentration term factored into the equation adequately accounts for the dependency of the reaction rate on reactant concentration [12]. Using these three quantities the activation overpotential can be calculated.

For each point on the polarization curve, the cell voltage is taken as the solid phase potential assigned to the cathode since the anode is arbitrarily chosen as the ground. The current density is obtained in the post processing by integrating the normal current density on the cathode boundaries and normalizing it by the channel volume (Fig. 3) to find the geometry that produces the highest power density per volume. This demonstrates which design is the most suitable as a compact power source for portable devices. To be consistent with the results reported in the literature [9], the output current has also been normalized by electrode surface area (Fig. 4).

4. Implementation in COMSOL

The graphical user interface and pre-programmed modules allowed for efficient testing of different geometries and electrode configurations since the subdomain and boundary conditions could be rapidly created for different designs.

4.1 Solution Procedure

The governing equations are solved by the finite element method using COMSOL multiphysics. A parametric sweep was used to calculate the current density at different cell voltages. Since the Butler-Volmer reaction

kinetics expression creates bidirectional coupling between the potential and convection-diffusion equations, the two must be solved simultaneously in order to obtain an accurate solution. However, the coupling of these equations results in a non-linear equation system for which it is difficult to obtain convergence from COMSOL's non-linear solver. Therefore, instead of solving the modules in a coupled manner, an iterative solution procedure was implemented by using the stationary segregated solver. This method allows for a stable solution procedure with reduced memory requirements while still accounting for the coupling between the physics modules. To keep the solution time reasonable and ensure a robust solution procedure, the direct UMFPACK linear system solver was used for all modules.

4.2 Meshing

It was found that a very fine mesh pattern was required around the electrodes to obtain convergence and ensure that the solution is accurate and mesh independent. This refinement was made for two reasons: first to allow for accurate flux computation when calculating the current density, and second to ensure the numerical stability of the convection-diffusion equation which can become unstable in the presence of steep concentration gradients.

The model was solved on a 64-bit Windows Vista platform, with an Intel Xeon 2.26 GHz quad-core processor. Peak memory usage was observed to be about 3 GB. Run-times to complete a polarization curve with 9 points were about 3 hours.

5. Results

The concentration distributions of the oxidant in each of the channel designs are shown in Figure 2. The mixing region is visible along with a depletion region near the electrodes where the reactants have been consumed due to the electrochemical reactions. Polarization curves for the three geometries examined are presented in Figures 3 and 4. It is observed that the high aspect ratio channel consistently has the highest current density for any cell voltage.

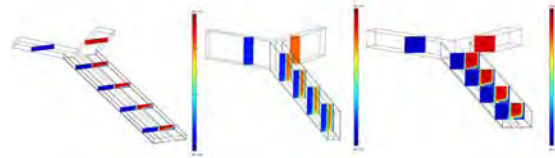


Figure 2. Concentration distributions of oxidant in the square channel and high and low aspect ratio channels

When the current density is normalized by the channel volume, the high aspect ratio geometry shows the best performance because it has the largest electrode area. However, even when the current density is normalized by the electrode area, the performance of the high aspect ratio design is better because the spacing of the electrodes is smaller which means that the proton electrolyte resistivity is reduced.

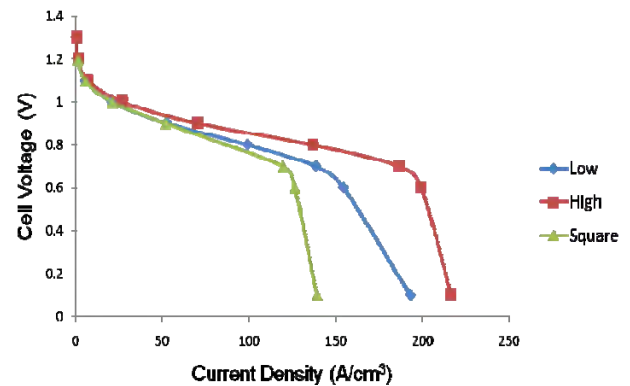


Figure 3. Polarization curves showing current density normalized by the channel volume

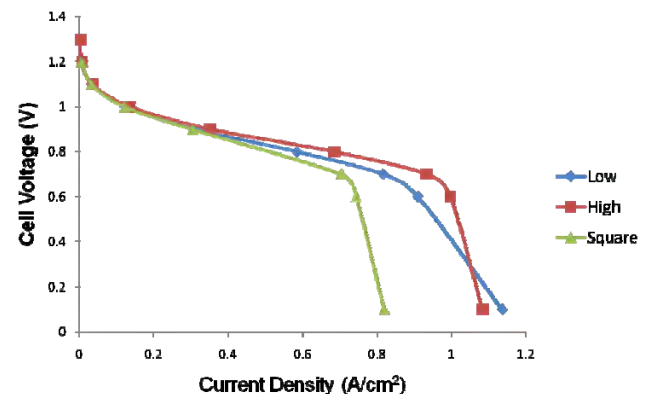


Figure 4. Polarization curves showing current density normalized by the electrode surface area

The square and low aspect ratio channels have the same electrode surface area. However, the low-aspect ratio channel exhibits higher performance. The smaller the height of the channel, the lower the growth rate of the mixing region. This ensures that the reactants remain closer to the electrodes where they can be readily used for electrochemical reactions. It is expected that the performance of the low aspect ratio channel could be further enhanced by extending the electrodes up to the maximum extent allowed by the mixing region.

6. Conclusions

An effective and efficient numerical modeling tool for the design of microfluidic fuel cells has been demonstrated using COMSOL. These simulations account for the key factors and parameters in fuel cell performance including fluid flow, reactant transport, electric fields and reaction kinetics. The efforts of this kind are invaluable for the commercialization of this technology since it is possible to test and refine different fuel cell designs rapidly at low cost.

The results show that higher performance is achieved by using the high aspect ratio channel. In this design, the larger electrodes and closer electrode spacing creates more active area and lower ohmic losses than in the other channels.

Future work will focus on testing additional geometries in order to find an optimal design.

7. References

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9. Appendix

Parameter	Anode Flow	Cathode Flow
Density, ρ	1000 kg/m ³	
Dynamic viscosity, μ	0.001 Pa*s	
Faraday constant, F	96485.34 C/mol	
Cell temperature, T	298 K	
Universal gas constant, R	8.314 J/(mol*K)	
Ionic conductivity, σ	12 S/m	40 S/m
Ref. Concentration, c_{REF}	210 mol/m ³	0.5 mol/m ³
Diffusion coefficient, D	8.3e-9 m ² /s	8.3e-9m ² /s
Charge transfer coefficient, α	0.5	0.5
Number of electrons transferred, n	2	4
Exchange current density, i_0	3.82e5 A/m ³	100 A/m ³
Reversible potential, $E_{REVERSIBLE}$	1.48 V	0 V
Inlet concentration, c_0	210 mol/m ³	0.5 mol/m ³