A Computational Study to Overcome Mass Transfer Limit in Microfluidic Fuel Cell

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ABSTRACT

Membraneless micro fuel cells have eliminated some technical issues related to membrane-based fuel cells such as dry-out at anode and flooding at cathode. However, performance of membraneless micro fuel cell using dissolved oxygen as oxidant is mainly restricted by low concentration of oxygen which cannot provide sufficient driving force to replenish depletion boundary layer at electrode surfaces. Consequently, electro-catalytic activity on cathode is weak. The goal of this work is to manipulate depletion boundary layer to minimize mass transfer limitation on electrodes.

Chemical activity limitation on cathode can be addressed by (1) using high oxygen concentration as oxidant, (2) using three stream laminar flows, and (3) using multiple inlets or outlets. A new design by combing multiple inlets or outlets with tapered electrode channel is proposed and studied in this work.

Computational simulation will be performed to report improved performance with various design configurations in terms of fuel utilization in variation with flow rate. With conventional micro fuel cell, fuel utilization has agreed well with experiments. Significance of results is to provide design rules – evidence to promote clean micro power source.

Keywords: membraneless fuel cell, microfluidics, mass transfer limit, cfd simulation

1 INTRODUCTION

Fuel cell technology promises to be a clean power source with broad applications in many industries including transportation as well as stationary and portable power generation [1,2]. For examples, solutions are needed to allow hybrid vehicles to be a viable substitute to combustion engine vehicles. Fuel cell technology can be the energy storage device that allows hybrid vehicles to compete with today's combustion engines and be the bridge to the next generation technology. Since fuel cells can produce large amount of clean energy for small components, this technology will also be the way to improve storage devices that can bridge the gap between battery technologies. Unlike the standard battery that has a cost penalty associated with the use of large batteries to gain higher energy content, fuel cells have the potential to provide much longer duration per weight and volume. Thus huge gains can be made in system energy density by implementing fuel cells.

Five major types of fuel cells are differentiated by their electrolytes, namely, PEMFCl, PAFC, AFC, MCFC and SOFC [3]. Among all types of fuel cells, the PEM fuel cell can achieve high power density (the ratio of electrical power output to the size of the system generating that power), and operates at relatively low temperatures. PEM fuel cells also respond quickly to the transient power requirements, which make them extremely suitable for automotive and stationary backup power applications. The PEM fuel cell is believed to be a promising replacement for combustion engines because of its high efficiency and low emissions. However, PEM fuel cells require proper heat and water management to meet performance targets - high efficiency, high power density, and low cost. The core technology of a PEM fuel cell is the polymer electrolyte membrane. This membrane must exhibit high conductivity – the ability to conduct protons through it. The membrane conductivity relies heavily on its water content - hydration. If the fuel cell operates too dry, low water content will reduce the membrane conductivity, resulting in a loss in efficiency. If the membrane operates too wet, flooding will occur, which impedes hydrogen and oxygen from getting to the membrane's catalyst surface, leading to a degraded cell performance. Another serious problem with the membrane-type PEM fuel cells is the fuel crossover from one electrode to another through the membrane. Due to the mixing of fuel with the oxidant at cathode, the chemical reaction of reduction is no longer restricted to the proper electrode and it will therefore lower the cell performance.

The proposed laminar-flow-based, membrane-less micro fuel cell takes advantage of the nature of micro laminar flows to maintain separation of the fuel and oxidizer streams and thus eliminates the necessity for a membrane [1,2]. As a result, water management will be simplified and fuel crossover can be prevented by adjusting the flow rate of each stream to limit the diffusion zone. Since the fuel and oxidant can be placed in the same channel, the size of fuel cell can be designed to be smaller to simplify the design and cut the cost. Compared to the gaseous fuels the liquid fuels have higher energy density, and the micro-fluidic fuel cells take further advantage of using liquid fuel to improve its viability in portable power applications. Although many efforts are directed to develop and optimize micro fuel cells as a potential power source, the current designs showed relatively poor fuel utilization (<10%) and relatively low current densities (8mA/cm^2). One of major challenges among these efforts is to identify the fuel cell performance limiting factors.

Studies showed that two physicochemical phenomena - depletion and diffusion in a membrane-less micro-fluidic fuel cell will govern the conversion of chemical energy to electrical power and mass transport of species [1,5,6]. As shown in Figure1, when the fuel stream and the oxidant stream enter the channel, the mixing of the two streams occurs at the liquid-liquid interface due to the diffusion which is perpendicular to the flow direction. The degree of mixing will depend on the diffusivity of species and the time that the two streams are in diffusion contact. During the operation process of membrane-less micro-fluidic fuel cells, mass transfer for the species of hydronium ions (H+) to the cathode is not a limiting factor due to its high diffusivity ($9.31x10^{-5}$ cm^2/s). However, due to low diffusivity of oxygen ($2x10^{-5}$ cm2/s) and low solubility (1.14Mm), not enough oxygen is supplied to the cathode by diffusion through a micro-scale aqueous stream. As a result, the concentrations of oxygen are low, making replenishment of cathodic depletion zones inefficient. Oxygen (dissolved) is often preferred to use as the oxidant because of its availability from the atmosphere for most fuel cell applications. Formation of depletion zone results from the depletion of reactants when a heterogeneous reaction occurs at the reactive surface. Without depletion zone being replenished sufficiently, a lower concentration of the reactant (H+, O2) occupies the region directly next to the cathode than the concentration of reactant in the bulk region, leading to a lower conversion rate and a degraded cell performance.

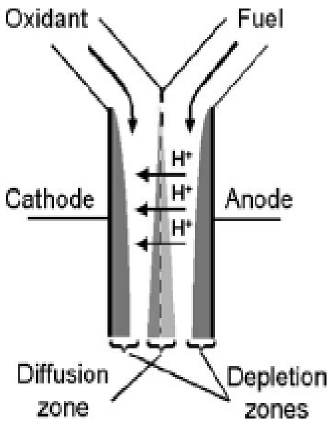

Figure 1: Separation of fuel and oxidant [2].

In order to overcome mass transfer limitation of oxygen at electrode surfaces, the transport rate of oxygen to reactive surfaces can be enhanced by redesigning the micro fuel cell: (1) using three inlets of fuel and oxidant, (2) increasing oxygen concentration, (3) using one more electrolyte solution between fuel and oxidant streams. In this paper, a membraneless micro fuel cell using the multi-stream laminar flow will be conducted and numerical analysis using computer software will be used to optimize micro-fuel-cell designs and cell performance.

2 METHODS

Model based on computer simulation is initiated early on in a fuel cell development cycle due to its significant role in fuel cell design and development process. It helps designers determine how well candidate systems perform and whether to further fabricate and test the new design.

Based upon the commercial CFD software package, FLUENT, a three-dimensional numerical simulation and analysis of the fuel cell were conducted to study the fuel cell performance. Modeling of electrochemical reactions, flow kinetics, and species transport is developed and combined into the CFD software with appropriate boundary conditions. Formic acid (HCOOH) is used as the fuel. Oxygen (O2) is dissolved in sulfuric acid so that aqueous solution of sulfuric acid saturated with oxygen is used as the oxidant. The flow streams of Fomic acid and oxygen are assumed incompressible and steady with uniform properties. Due to the moderate liquid velocity, the flow is laminar and is governed by standard continuity and Navier-Stokes equations without body forces as:

$$\frac{\partial u_i}{\partial x_i} = 0 \qquad (1)$$

$$u_j \frac{\partial u_i}{\partial x_j} = -\frac{1}{\rho}\frac{\partial P}{\partial x_i} + \nu \Delta u_i \qquad (2)$$

Conservation for chemical species transport is governed through a convection-diffusion equation for the ith species:

$$\rho u_j \frac{\partial Y_i}{\partial x_j} = \rho D_i \Delta Y_i + R_i \qquad (3)$$

where Yi, is the local mass fraction of species i, Di is the diffusion coefficient for species i in the mixture and Ri is the net rate of production of species i by chemical reaction.

During the chemical reaction, chemical species is assumed to be deposited on surfaces only and hence chemical reaction is treated as surface reaction. The formic acid releases electrons and protons at the anode:

$$HCOOH \text{ -> } CO_2 + 2H^+ + 2e^- \qquad (4)$$

The protons, across the interface, diffuse to the oxidant stream so that the oxygen reacts with protons to produce water:

$$O_2 + 4H^+ + 4e^- \text{ -> } 2H_20 \qquad (5)$$

The rate constant in a chemical reaction is given by the Arrhenius equation:

$$k = Ae^{-E_a/RT} \qquad (6)$$

where A is the pre-exponential factor, Ea is the activation energy, R is the gas constant, and T is the temperature.

3 RESULTS AND DISCUSSION

This paper discusses a membraneless micro fuel cell using the multi-stream laminar flow to separate the fuel and oxidant streams. One of the key problems in the membraneless micro fuel cell continues to be the overlap of fuel and oxidant. Extensive studies have shown that in multi-stream laminar flow, diffusion which is transverse to the flow direction causes the mixing of the two streams. The Schmidt and Peclet numbers are dimensionless values that allow for a quantitative understanding of the transport issues associated with fluid flow in rectangular ducts similar to the ones studied here [2,5]. The Schmidt number allows for a numerical comparison of the kinematic diffusivity with mass diffusivity, $Sc = v/D$, where v is the kinematic viscosity and D is the mass diffusivity of the species of interest through a particular solution. In our simulations, the Schmidt number is much greater than 1 causing the viscosity to affect diffusion more rapidly than concentration affects the exposure of the concentration boundary layer to a linear velocity profile. The degree of mixing depends on the value of Peclet number defined by $Pe = UH/D$ [4, 5], where U is the mean velocity and H the channel height. The low diffusivity and concentration make the concentration flux toward the surface of cathode be small and thus the thickness of concentration boundary layer grows along the channel. One can see that the concentration boundary layer of diffuse oxygen solution at cathode is quite small even at $Pe=10^3$ as shown in Fig.s1,2.

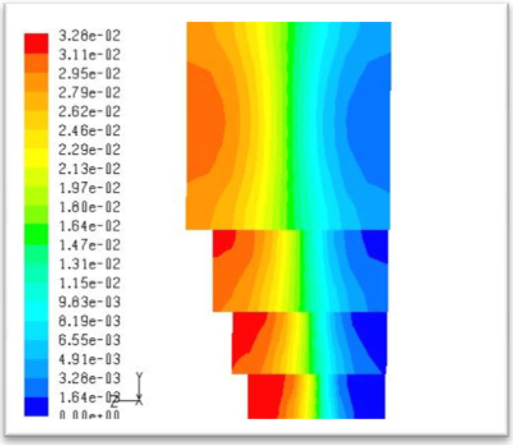

Figure 2: O_2 Concentration at $Pe=10^3$

By operating the laminar flow fuel cell discussed here at a high Peclet number we reduce the interface layer [2,5]. The performance of the membraneless fuel cell system can be affected by the hydrodynamic stability of the flowing streams. Fuel crossover by diffusion occurs with slower flow rates, resulting in a mixed potential at the cathode and lower cell performance. The operating velocity range depends on the geometry of the system and composition/concentration of fuel and oxidant streams. In our simulation we first increased the inlet velocity to increase the Peclet number. By operating at high Peclet and Schmidt numbers (i.e. at $Pe \geq 10^4$ and $Sc >> 1$) the concentration boundary layer can be pressed close against the wall and fuel crossover can be prevented simultaneously[2,7]. The scaling analysis also suggests that reducing the dimensions of the channel will decrease the width of the depletion region while keeping all other process variables constant. The thickness of concentration boundary layer decreases with increases in the Pe, so the cell performance should be raised simultaneously as demonstrated in Fig. 3 for the cases $Pe=10^4$. The optimum flow rates would, therefore, provide little to no fuel crossover while yielding high fuel and oxidant consumption.

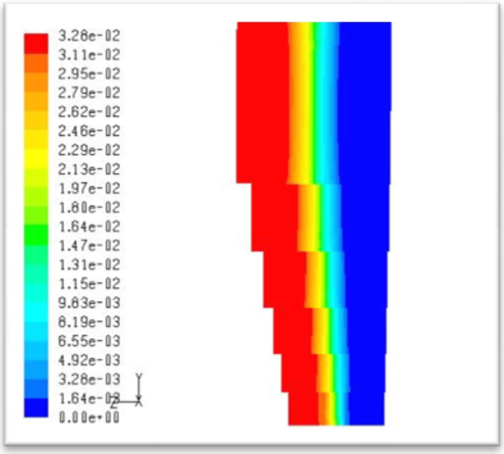

Figure 3: Formic Acid Concentration at $Pe=10^3$

It can be proposed that the performance of such a membraneless fuel cell is limited by the cathode. If the cell performance is limited by the cathode then the process can be enhanced profoundly if the concentration of oxygen in cathodic stream can be increased to raise concentration flux or the exchange current density at the cathode can be made as high as possible[1]. This limitation of insufficient cathodic concentration can be overcome by adding a proton source such as sulfuric acid to the cathode and/or anode stream, thus providing a supply of protons closer to the cathode.

In order to develop new micro fuel cell designs, the performance for several assigned values of aspect ratio against inlet velocity was demonstrated. Fig. 4 and Fig. 5 show that aspect ratios of 0.25 and 4 have different concentration profiles. A smaller aspect ratio also indicates

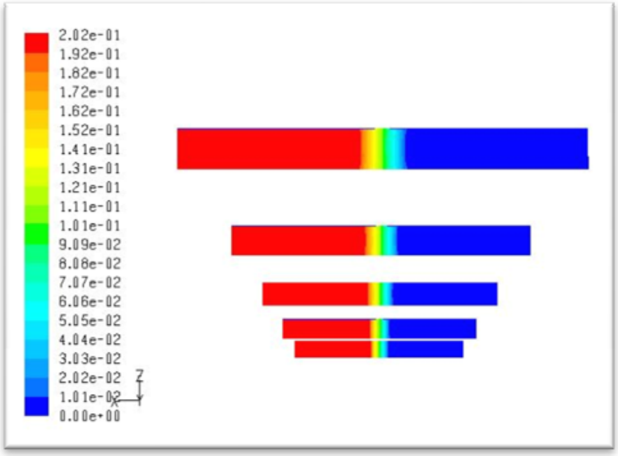

Figure 4: Formic Acid Concentration At Aspect Ratio 0.25

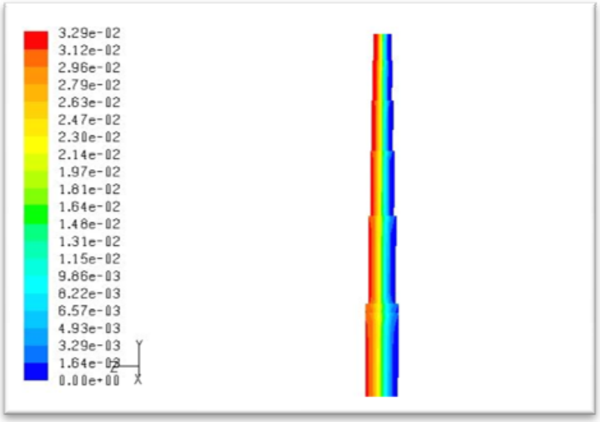

Figure 5: Formic Acid Concentration At Aspect Ratio 4

smaller cross-sectional area profiles. A large aspect ratio would require a large inlet velocity. A system can be designed to operate at a lower inlet velocity in a smaller system to achieve the same performance. Another studied geometry considered was three inlets. The fuel, oxidant, and electrolyte solution (here we use dilute sulfuric acid) enter the channel from the inlets and continue to flow in parallel without turbulent mixing. Adding a third stream containing only electrolyte between the fuel and oxidant streams could also enhance the conversion efficiency by forcing the fuel stream to be close in size to the concentration boundary layer thickness. Previous work tried to reduce the area of the electrodes at both anode and cathode to avoid the overlap of the diffusive mixed region with the electrodes [1]. Here we introduce a third channel containing only electrolyte solution between the fuel and oxidant streams. Directly contact and reaction between the fuel and oxidant can be prevented by formation of three streams laminar flow. By controlling the flow rate of this channel, the performance of the fuel cell can be studied. Increasing the flow rate of the middle stream decreases the crosslink of the fuel therefore the potential. In contrary, increasing the flow rate can also widen the distance between the fuel and oxidant, and decrease the diffusive rate of the H+ generating at the anode across the middle stream therefore decreasing the potential of the cell. The electrolyte we used can also increase the concentration of the H+ but simultaneously also decrease the gradient of the concentration. Considering these reasons, an optimum flow rate can be determined.

4 CONCLUSION

The CFD FLUENT simulations demonstrate the operation of a fuel cell based on multi-stream laminar flow. The proposed laminar flow, membrane-less fuel cell takes advantage of the laminar nature of micro flows to maintain the separation of fuel and oxidizer streams and thus eliminates the necessity for a membrane. Our goal is to design a device that will optimize the microfludic system by minimizing the size and maximizing the current density with significantly high fuel efficiency. By removing the membrane the complexity of the fuel cell design will be reduced resulting in no membrane “dry-out”, a higher temperature tolerance, and no maintenance of the membrane. With the understanding of transport phenomena and operation of the laminar flow-based microfuel cell, a high performance laminar flow-based microfuel cell can be constructed with the design criteria of a Schmidt number greater than one, Peclet numbers greater than 10^4 and an aspect ratio much less than one. Preliminary simulations suggest that the fuel cell performance is limited by the transport of reactants through the concentration boundary layer to the electrodes and by the low concentration of oxidant in the cathode stream. By using high oxygen adsorption capability yet good ionic conductivity and channel designs, improvement in the performance is expected. While the multi-stream laminar flow concept discussed in this paper is promising, more laboratory work needs to be conducted in order to verify assumptions made.
Preliminary results suggest that the fuel cell performance is limited by the transport of reactants through the concentration boundary layer to the electrodes and by the low concentration of oxidant in the cathode stream. Fuel cells are expected to be a potential power sources for a wide variety of applications. The proposed laminar flow, membrane-less fuel cell takes advantage of the laminar nature of micro flows to maintain the separation of fuel and oxidizer streams and thus eliminates the necessity for a membrane. Successful development of the fuel cell simulation is expected to serve as the first step toward an improved economic optimization in fuel cell design. Comparison can be made with other fuel cell systems such as those based on PEM membranes.

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