

Engineering Model for Coupling an Electro-osmotic Fuel Micropump with a Miniature Direct Methanol Fuel Cell

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Abstract

This paper presents a theoretical study of an active fuel delivery system for a miniature liquid feed direct methanol fuel cell using an electro-osmotic micro pump. A higher methanol flowrate, with the help of a pump in an active system, generally can improve performance. In the process of the study, approximate expressions for pressure drop and fuel flowrate at the anode of the direct methanol fuel cell using a steady state model that considers conservation of mass, momentum and species together with the electro-kinetics, are derived. This model is used to illustrate the favorable scaling of EO pumps with direct methanol fuel cells for methanol delivery.

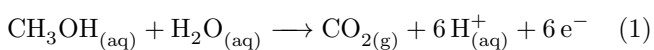
Keywords

Direct Methanol Fuel Cell, Electro-osmotic, Micro Pump, Fuel Cell Model

Introduction

Direct methanol fuel cells (DMFC) are considered to be a replacement for batteries in portable electronic devices such as cell phones and laptops, and in the future, a probable solution for automotive and transportation systems. That is because of the high volumetric energy density of liquid methanol and its easier storage and transportation compared to hydrogen, as the fuel in other fuel cells.

Passive fuel delivery systems have been used in typical DMFCs due to their simplicity, small volume and minimal power consumption. However, they depend on operating conditions such as temperature, pressure and concentration gradients, and lack a method for management of produced gas, as one mole CO₂ gas is created for every mole of liquid methanol at the anode of the DMFC:



The produced CO₂, if not managed, can block the passage of fresh methanol fuel to the reactions sites, and there-

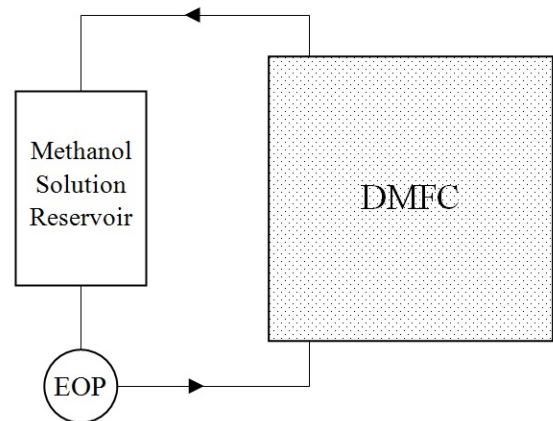


Fig. 1: Schematic of the system showing the position of electro-osmotic pump in system.

fore lower the performance of DMFC. A forced flow can create a disturbance in the bulk solution and effectively remove and minimize the accumulation of CO₂ bubbles at the anode surface and improve the performance [1]. Active systems are more reliable and result in higher performance and power density at the expense of a fraction of DMFCs power. The basic reason that holds back active systems is the incapability of the present classical miniature low-power pumping technologies. However, it has been shown that electro-osmotic (EO) pumps can deliver the required flowrate using only a small fraction of cell power [2].

In the present work, the coupling of an EO pump with a miniature DMFC in an active fuel delivery system is studied, as shown in Figure 1, and the method of calculations of the pressure drop and flowrate is considered in detail.

Electro-osmotic Pump Theory

Electro-osmosis is an electrokinetic effect which can be used for pumping in small channels, where the surface to volume ratio is large. EO flow is the bulk motion of an electrolyte caused by Coulombic interaction of external electric fields and the charges of a thin electric double layer (EDL),

denoted the Debye layer.

Some of the properties which make EO pumps highly suitable for DMFC applications can be named as having no moving parts and being capable of generating high flowrate and significant pressure drop per device volume [2]. In addition, these pumps have a fairly wide range of working electrolytes including deionized water and methanol.

The most important specifications which characterize the performance of a micro pump are maximum flowrate, maximum back pressure and efficiency. These parameters are analytically modeled for an EO porous micro pump by Yao and Santiago [3]. They found the flowrate for a general pressure load to be

$$Q_{eo} = A_{eo} \frac{\psi_{eo}}{\tau} \left[-\frac{a^2}{8\mu_l} \frac{\Delta p}{L_p} - \frac{\varepsilon \zeta f}{\mu_l} \frac{V_{eff}}{L_p} \right] \quad (2)$$

where a , τ , ψ_{eo} , A_{eo} , and L_p are the pore radius, tortuosity, porosity, cross sectional area, and thickness of the porous media, respectively. Also μ_l and ε are the viscosity and permittivity of the liquid, and ζ is the zeta potential. The effective voltage, V_{eff} , is the applied voltage, V_{app} , minus the decomposition potential and ohmic loss between electrodes and porous materials. The non-dimensional factor, f , accounts for the effect of the EDLs finite thickness on the velocity profile in the pores.

Coupling Model

The anode flow field of the DMFC is to supply methanol solution through the anode diffusion layer to the anode catalyst layer and transport out CO_2 from the cell. Hence, the flow in the flow field is in the form of gas-liquid two phases. Since the two-phase flow behavior in the flow field affects not only the mass transport of methanol to the anode CL, but also the removal of CO_2 from the cell, it is directly related to cell performance [4].

Carbon dioxide bubbles produced in the methanol oxidation reaction enter the anode channel and disturb the flow of the methanol-water solution. The direct effect of gaseous bubbles is a dramatic acceleration of the flow. Experiments show that in typical situations the outlet flow velocity exceeds the inlet velocity by an order of magnitude [5]. This is easy to understand as gas density is much lower than the density of liquid and simple mass conservation prescribes that due to an increasing concentration of gaseous bubbles, the two-phase flow must accelerate.

The effect of gaseous bubbles can, however, be neglected in two cases: (i) when the cell operating temperature is low (below 30°C) and (ii) when the cell current is small. At low temperature the solubility of CO_2 in water is high and the product CO_2 remains dissolved in water. At small currents, the rate of bubble formation is small.

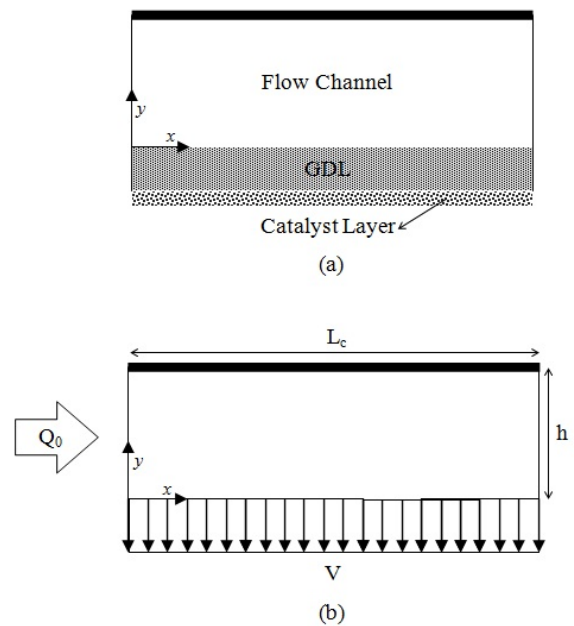


Fig. 2: Schematic (a) and model used in this paper (b) of the anode side of a DMFC.

The approach used in this paper is that the DMFC is considered to be working at a constant current density and then the required flowrate and resulting pressure drop are estimated. Using these two main parameters, other parameters to design a suitable electro-osmotic micro pump can be selected.

The flowrate is found by calculating the amount of consumed methanol, the concentration of methanol solution and also considering methanol crossover phenomenon. To estimate the pressure drop, a reduced two dimensional model for anode of a DMFC, shown in Figure 2, is used.

In this model, it is assumed that the methanol solution is fed to the flow channel at constant flowrate Q_{eo} and the consumed solution is extracted from the bottom plate of the channel with uniform velocity of V . The main assumptions in the mathematical formulation are the following: (i) steady-state operation, (ii) carbon dioxide is assumed to be dissolved in the liquid phase, and (iii) isothermal condition. The flow is fully developed at the inlet of the channel and due to low Reynolds number, the governing equations are considered to be Stokes equations.

The continuity equation is automatically satisfied by introducing Lagrange's stream function $\psi(x, y)$ such that

$$u_x = -\frac{\partial \psi}{\partial y}, \quad u_y = \frac{\partial \psi}{\partial x} \quad (3)$$

The advantage of using the stream function is that, instead of a system of three PDEs for the three unknown fields, u_x , u_y and p , a single PDE for the new dependent variable, ψ has to be solved. The price paid is that

the highest derivatives of the governing equation are now fourth-order instead of second-order

$$\nabla^4 \psi = \frac{\partial^4 \psi}{\partial x^4} + 2 \frac{\partial^4 \psi}{\partial x^2 \partial y^2} + \frac{\partial^4 \psi}{\partial y^4} = 0 \quad (4)$$

Separating the horizontal from the vertical dependence and stipulating a power-law functional dependence on x , a solution to Eq. (4) is presumed of the form

$$\psi_g = x^\lambda F(y) \quad (5)$$

Applying the operator ∇^4 to the above solution yields

$$\nabla^4 \psi_g = \lambda(\lambda-1)(\lambda-2)(\lambda-3)x^{\lambda-4}F(y) + 2\lambda(\lambda-1)x^{\lambda-2}F''(y) + x^\lambda F''''(y) = 0 \quad (6)$$

Due to the Stokes flow Eq. (4), the only admissible values of λ are 0 and 1. For both values, it results in the simple fourth-order ODE

$$F''''(y) = 0 \quad (7)$$

Considering the geometry of the problem, a linear combination of both cases is supposed to be the general solution

$$\psi(x, y) = (ax-1)F(y) = (ax-1)[c_0 + c_1y + c_2y^2 + c_3y^3] \quad (8)$$

with the boundary conditions

$$\text{at } y=0 \begin{cases} u_x = 0 \\ u_y = -V \end{cases}, \quad \text{at } y=h \begin{cases} u_x = 0 \\ u_y = 0 \end{cases} \quad (9)$$

and

$$Q_{eo} = b \int_0^h u_x|_{x=0} dy \quad (10)$$

in which b is width of the channel.

By substituting the general solution into these boundary conditions, one can find the final solution

$$u_x = \left(\frac{Q_{eo}}{bV} - x \right) \frac{6V}{h} \left[\frac{y}{h} - \left(\frac{y}{h} \right)^2 \right] \quad (11)$$

$$u_y = V \left[-1 + 3 \left(\frac{y}{h} \right)^2 - 2 \left(\frac{y}{h} \right)^3 \right] \quad (12)$$

Integrating the x-momentum equation between inlet and outlet results in the pressure drop along the channel

$$\Delta p = \frac{12\mu V}{h^3} \left(\frac{Q_{eo}L_c}{bV} - \frac{L_c^2}{2} \right) \quad (13)$$

By adding the assumption of constant concentration of methanol in the channel, flowrate of the consumed solution can be found

$$Q_{con} = \frac{i_{eq}A_{FC}}{6F} \frac{M_{MeOH}}{\rho \omega_{MeOH}} \quad (14)$$

in which M_{MeOH} , ω_{MeOH} and F are methanol molecular mass, methanol mass fraction of solution and Faraday constant, respectively. Also A_{FC} is the fuel cell active area and i_{eq} is the equivalent current density of DMFC to account for methanol crossover effects

$$i_{eq} = i + i_{cross} \quad (15)$$

Methanol crossover happens when methanol molecules diffuse through the membrane and are directly oxidized by oxygen on the positive electrode [6]. Methanol crossover from the anode to the cathode is a very serious problem that severely reduces cell voltage, current density and fuel utilization, and hence cell performance [7]. Polymer electrolyte membranes offer a high resistance to crossover of gases. However, the mechanism of proton transport in these membranes is inherently related to water molecules, and PEM membranes are highly permeable to water. Methanol and water molecules are similar and hence methanol easily permeates these membranes.

On the cathode side, permeated methanol reacts directly with oxygen; the presence of catalyst particles facilitates the direct combustion. This parasitic reaction consumes methanol and lowers the amount of oxygen available for useful electrochemical conversion [8]. Thus, any realistic model of DMFC should include crossover.

It is convenient to introduce the equivalent crossover current density. To calculate i_{cross} it is assumed that (i) methanol is transported through the membrane due to diffusion and electro-osmosis and (ii) the diffusion coefficient of methanol in the membrane D_m is constant [9]. The latter assumption is justified since in DMFC the membrane is fully hydrated. Under these assumptions [10]

$$i_{cross} = \frac{\beta}{1+\beta} i_D \left(1 - \frac{i}{i_D} \right) \quad (16)$$

in which

$$\beta = \frac{D_m l_b}{D_b l_m} \quad (17)$$

is the crossover parameter and

$$i_D = \frac{6FD_b c_h}{l_b} \quad (18)$$

is the methanol limiting current density. D_b , l_b , l_m and c_h are methanol diffusion coefficient in the anode backing layer, backing layer thickness, membrane thickness and methanol molar concentration in the channel, respectively.

Thus the uniform solution consumption speed at the bottom plate of the channel is found to be

$$V = \left[i + \frac{\beta}{1+\beta} i_D \left(1 - \frac{i}{i_D} \right) \right] \frac{A_{FC}}{6Fbh} \frac{M_{MeOH}}{\rho \omega_{MeOH}} \quad (19)$$

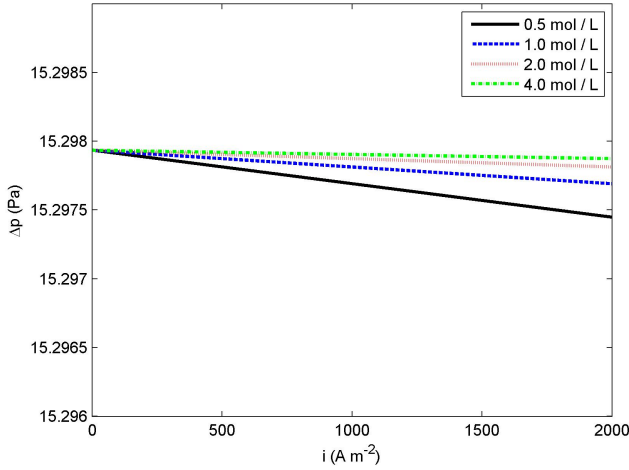


Fig. 3: Effect of methanol concentration on predicted pressure drop across the anode with inlet flow rate of 100 μlpm .

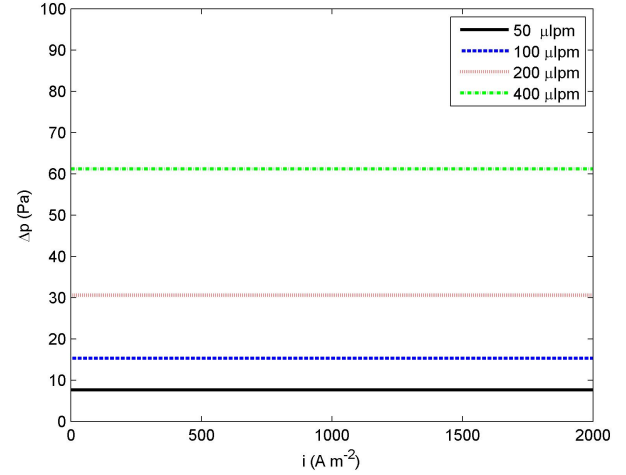


Fig. 4: Effect of inlet flow rate on predicted pressure drop across the anode with methanol concentration of 1 mol/L .

TABLE I: DMFC parameters and conditions.

Parameter	Value
Fuel cell electrolyte	Nafion 117
Gas diffusion layer	350 μm E-Tek anode
Active area	2 cm^2
Anode channel dimensions	750 μm \times 500 μm \times 13.1 cm
Methanol concentration	0.5, 1, 2, 4 mol/L
Anode flowrate	50, 100, 200, 400 μlpm
Cathode Gas	Atmospheric air
Fuel cell temperature	50 $^\circ\text{C}$

By combining Eqs. (2) and (13) and solving for flowrate, an expression for flowrate of an EO pump coupled with a DMFC is achieved

$$Q_{\text{eo}} = \frac{[(3a^2L_c^2/4h^3)V + \varepsilon\zeta fV_{\text{eff}}/\mu_l]}{[\tau L_p/A_{\text{eo}}\psi_{\text{eo}} + 3L_c a^2/2bh^3]} \quad (20)$$

in which should be replaced from Eq. (19).

Results and Discussion

The analytical model derived above was used to predict the effects of methanol concentration and solution inlet flowrate on pressure drop along the flow channel for a DMFC identical to the one used by Buie and Santiago [11, 12]. A summary of DMFC parameters and conditions is given in Table 1.

Figure 3 presents the predicted pressure drop plotted against current density for various methanol concentrations. It can be seen that methanol concentration has a relatively small effect on hydrodynamics in the anode, despite its strong effect on the electrochemical performance of the DMFC, which is in agreement with experimental results [11]. Pressure distribution along the channel also is independent of methanol concentration (not shown here).

This one phase model predicts a slight decrease in pressure drop as current density in the DMFC increases. This was expected due to the small reduction in axial velocity along the channel because of the consumption from the bottom plate. But that is not the case in real. Two phase behavior of the flow results in accelerated flow and increased axial velocity and consequently increased pressure drop.

Changes in pressure drop due to different inlet flowrates is shown in Figure 4. These results are comparable to numerical predictions of the separated two phase flow model of Buie and Santiago [12]. The different base scales for pressure drop in equal flowrates can be explained by the fact that the current model is two dimensional and does not capture the effects of channel's side walls on pressure drop.

Conclusion

With the purpose of improved performance and better control, an EO micro pump is coupled and sized for a miniature DMFC. To achieve that, it is necessary to find approximate expressions for required flowrate and the resulting pressure drop in the path of the methanol solution, which are derived analytically, considering a reduced two dimensional model of the anode of a DMFC with a serpentine flow channel. The method is explained step by step and the derived expressions are compared with available experimental and numerical results.

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