



Direct methanol fuel cells with streamline graded structure under ultra-low fuel stoichiometry condition



Seunghun Jung*, Chao-Yang Wang

Electrochemical Engine Center (ECEC), Department of Mechanical and Nuclear Engineering, The Pennsylvania State University, University Park, PA 16802, USA

HIGHLIGHTS

- Severe non-uniformities in a DMFC are predicted under ultra-low fuel stoichiometry condition.
- This paper identifies the controlling parameters of the methanol transport in a DMFC.
- Two strategies called 'streamline graded structures (SGSs)' to mitigate non-uniformity are proposed.
- Computational results show SGS models have 10% improved performance compared to the baseline model.

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ABSTRACT

Operating a direct methanol fuel cell (DMFC) with ultra-low fuel stoichiometry is desirable to build a compact portable power system. Through 3D computational modeling with statistical analysis, severe non-uniformity of fuel concentration leading to high methanol crossover in the inlet region and poor fuel supply in the outlet region is predicted under ultra-low fuel stoichiometry condition, which causes large voltage loss or even cell shut-down. After identifying controlling parameters of methanol transport, this paper proposes streamline-graded structures (SGS) of the anode channel to mitigate anode fuel distribution non-uniformity and to boost cell performance and fuel efficiency together. Computational results show that streamline-graded structures achieve about 10% of voltage gain and 3% of fuel efficiency improvement compared to the conventional DMFC design by mitigating anode non-uniformity.

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1. Introduction

In order to develop a compact, portable direct methanol fuel cell (DMFC) system, there are several objectives to achieve, such as high energy density, small system size and high fuel efficiency. First, energy density of the DMFC system must be increased by using highly concentrated fuel. Many DMFCs carry a diluted fuel solution which consists of water and methanol. Although cell operation with dilute solution has benefits of reducing methanol crossover and increasing cell voltage, it is not optimal for development of portable DMFCs because dilute solution lowers energy density of the entire DMFC system. As water is produced in the cathode catalyst layer by oxygen reduction reaction (ORR), it is theoretically possible to achieve a water-neutral condition to operate a DMFC without

external water supply to the anode side. Blum et al. [1] first proposed this water-neutral condition and they concluded that carrying pure liquid methanol is theoretically possible when the water transfer coefficient (α) is equal to $-1/6$. However, supplying pure methanol to a DMFC causes severe methanol crossover and it is difficult to uniformly supply fuel to a DMFC with low fuel stoichiometry. Even though a DMFC system carries a pure methanol tank, it must dilute pure methanol internally with produced water.

Balance of plant (BOP), occupying a large volume of a DMFC system, should be reduced also. The gas–liquid separator located at the anode outlet can be removed if CO₂ gas is vented through alternate routes. Conventional DMFCs use a pump to supply liquid fuel on the anode side. If anode flow rate is minimized, this pump size can be reduced and required power for pump operation can be reduced as well. Due to CO₂ production by methanol oxidation reaction (MOR) in the anode, a strong two-phase flow exists in the anode channel. This two-phase flow causes a large pressure drop by two-phase frictional loss and inertial loss. The CO₂ breathing type DMFC removes CO₂ directly to the ambient and almost pure liquid

* Corresponding author. Battery R&D, LG Chem Research Park, 104-1, Moonjiddong, Yuseong-gu, Daejeon 305-380, South Korea. Tel.: +82 10 8443 5214; fax: +82 42 862 1981.

E-mail addresses: stratus76@hotmail.com, stratus760@gmail.com (S. Jung).

flows in the anode channel, which reduces the required pumping power [2,3].

Maintaining ultra-low fuel stoichiometry is another way to construct a compact DMFC system and reduce manufacturing cost. When a DMFC operates with large fuel stoichiometry condition, redundant methanol which did not participate in anode reaction is lost to the cathode side by diffusion and electro-osmosis drag through the overall exchange membrane. This methanol crossover lowers the overall fuel efficiency. High fuel efficiency is particularly important for a portable system as it determines the total operational time of the system. The easiest way to minimize methanol crossover is to operate a DMFC with ultra-low fuel stoichiometry.

$$\nabla \cdot (\gamma \rho \vec{u} Y^k) = \nabla \cdot [\rho_l D_{l,\text{eff}}^k \nabla Y_l^k + \rho_g D_{g,\text{eff}}^k \nabla Y_g^k] - \nabla \cdot [(Y_l^k - Y_g^k) \vec{j}_1] + S^k \quad (1)$$

When the vapor–liquid equilibrium of methanol is assumed in the anode by Henry's law, gas and liquid methanol concentration are related as

$$c_l^{\text{MeOH}} = c_g^{\text{MeOH}} k_H^{\text{MeOH}} \quad (2)$$

The following relationship can be established by multi-phase mixture model theory.

$$\rho Y^{\text{MeOH}} = \rho_l Y_l^{\text{MeOH}} s + \rho_g Y_g^{\text{MeOH}} (1-s) \quad \text{where} \quad \begin{cases} \rho Y^{\text{MeOH}} = c^{\text{MeOH}} M^{\text{MeOH}} \\ \rho_l Y_l^{\text{MeOH}} = c_l^{\text{MeOH}} M^{\text{MeOH}} \\ \rho_g Y_g^{\text{MeOH}} = c_g^{\text{MeOH}} M^{\text{MeOH}} \end{cases} \quad (3)$$

And, theoretically, it is ideal to operate a DMFC near anode limiting current density regime where methanol crossover is almost zero, which enables the cell to achieve maximum performance with maximum fuel efficiency. It is, however, not easy to achieve this ideal operating condition because fuel concentration may distribute in three dimensions non-uniformly.

When a DMFC operates at very low fuel flow rate, convective effect of methanol transport in the channel direction becomes weak. Instead, diffusive effect of methanol transport through the membrane electrode assembly becomes stronger and large amount of methanol may diffuse through the proton exchange membrane in the inlet region, causing severe methanol crossover there. In contrast, the outlet region may suffer from fuel depletion, which also degrades cell performance by increasing mass transport overpotential. Therefore, when liquid fuel is supplied from the inlet at ultra-low flow rate, some regions will operate with excessive fuel and some regions may suffer from fuel shortage. This is called 'fuel concentration non-uniformity'. Fuel concentration non-uniformity eventually leads to current density non-uniformity, temperature non-uniformity, and even cell shut-down. All of those non-uniformities are called 'anode non-uniformity'. It can be easily conjectured that the anode non-uniformity has a strong influence on the overall cell performance and fuel efficiency.

In this paper, we mathematically investigate the anode non-uniformity as well as its consequences on cell performance when a DMFC operates at ultra-low fuel stoichiometry. After identifying that, strategies of mitigating anode non-uniformity are introduced in order to improve both cell performance and fuel efficiency required for portable power sources.

2. Physics model

In order to analyze transport phenomena in a DMFC, previously developed multi-D DMFC model [4–6] is applied to the present study. Governing equations and constitutive relationships are summarized in Tables 1 and 2, respectively. Coupled PDEs (mass, momentum, species, proton transport, electron transport, and energy) are solved together with source terms. Cell dimension and simulation parameters are presented in Tables 3 and 4, respectively. As the present study focuses on methanol transport, the methanol transport equation for the multi-D model is revisited here. A general form of multi-phase species equation by M² model [7] can be expressed as follows:

Combining Eq. (2) and Eq. (3), methanol mass fraction can be found as follows

$$Y^{\text{MeOH}} = \frac{\rho_l}{\rho} \left(s + \frac{1-s}{k_H^{\text{MeOH}}} \right) Y_l^{\text{MeOH}} \quad (4)$$

Therefore, the methanol transport equation can be reformed from Eq. (1) as follows:

$$\nabla \cdot (\rho \vec{u} Y_l^{\text{MeOH}}) = \nabla \cdot \left[\rho_l \left(D_{l,\text{eff}}^{\text{MeOH}} + \frac{D_{g,\text{eff}}^{\text{MeOH}}}{k_H^{\text{MeOH}}} \right) \nabla \cdot Y_l^{\text{MeOH}} \right] - \nabla \cdot [(Y_l^{\text{MeOH}} - Y_g^{\text{MeOH}}) \vec{j}_1] + S^{\text{MeOH}} \quad (5)$$

The first term on the right hand side in Eq. (5) expresses the two-phase molecular diffusion. Since molecular diffusion of methanol is carried out by both liquid phase and gas phase, we define two-phase molecular diffusivity of methanol as follows:

$$D_{\text{eff}}^{\text{MeOH}} = \frac{\rho_l}{\rho} \left(D_{l,\text{eff}}^{\text{MeOH}} + \frac{D_{g,\text{eff}}^{\text{MeOH}}}{k_H^{\text{MeOH}}} \right) = \frac{\rho_l}{\rho} \left(D_l^{\text{MeOH}} s^n + \frac{D_g^{\text{MeOH}} (1-s)^n}{k_H^{\text{MeOH}}} \right) \varepsilon^n \quad (6)$$

As the value of k_H^{MeOH} is about 1191 in the room temperature, $D_{l,\text{eff}}^{\text{MeOH}}$ and $D_{g,\text{eff}}^{\text{MeOH}}/k_H^{\text{MeOH}}$ becomes similar order of magnitude. Note that two-phase molecular diffusivity of methanol is a strong function of both operating condition (liquid saturation) and material property (porosity). The liquid saturation shown above equation is defined as follows [7]:

$$s = \frac{V_l}{V_{\text{pore}}} = 1 - \frac{V_g}{V_{\text{pore}}} = \frac{\rho_g Y_{\text{H}_2\text{O}} - \rho_g Y_g^{\text{H}_2\text{O}}}{\rho_l Y_l^{\text{H}_2\text{O}} - \rho_l Y_{\text{H}_2\text{O}} + \rho_g Y_{\text{H}_2\text{O}} - \rho_g Y_g^{\text{H}_2\text{O}}} \quad (7)$$

And porosity is defined as,

$$\varepsilon = \frac{V_{\text{pore}}}{V} = \frac{V_{\text{pore}}}{V_g + V_l + V_{\text{pore}}} \quad (8)$$

The second term in Eq. (5) explains methanol transport by capillary force which becomes significant when the anode flow rate is large or methanol concentration is high. As the present study

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