Numerical investigation and optimization of vapor-feed microfluidic fuel cells with high fuel utilization

Yifei Wang^{a*}, Dennis Y.C. Leung^{a*}, Hao Zhang^b, Jin Xuan^c, Huizhi Wang^c

^aDepartment of Mechanical Engineering, the University of Hong Kong, Hong Kong, China

^bSchool of Mechanical and Electrical Engineering, Jiangxi University of Science and Technology, Ganzhou, China

^cInstitute of Mechanical, Process and Energy Engineering, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, UK

*Corresponding author: Dennis Y.C. Leung, Yifei Wang

Tel: (852) 3917 7911

Fax: (852) 2858 5415

Email: ycleung@hku.hk

Abstract

Vapor-feed microfluidic fuel cell (VF-MFC) has various advantages against the conventional liquid-feed microfluidic fuel cell, such as simpler fluidic management, higher fuel utilization, flow rate insensitiveness, and so on. To better understand the mechanisms behind its superiority and to further optimize its performance, a 3D isothermal numerical model has been developed in this work. The computational results agree very well with the previous and present experimental data, proving the validity of

the current model for the VF-MFC simulation. Through this model, it is found that the dissolved fuel in the VF-MFC is well-controlled within a thin boundary layer nearby the anode catalyst surface, which can not only satisfy the demand of anode oxidation reaction but also greatly alleviate the wastage of fuel. In this manner, the VF-MFC can achieve satisfactory power output and high fuel utilization at the same time. In addition, the boundary layer effect on electrolyte flow rate can keep the fuel concentration in the thin layer relatively stable at different flow rates, which may be the reason behind the insensitiveness of VF-MFC performance to electrolyte flow rate. To further improve its power output and fuel efficiency, effects of the fuel evaporation area and the anode open ratio have also been thoroughly investigated with the present model. It is found that an evaporation-reaction area ratio of 11.1 is sufficient for the present VF-MFC, while a smaller fuel evaporation area can lead to improved fuel utilization at the expense of lower power output. To improve both the fuel utilization and power output, the electrode area towards the channel outlet is increased while keeping the vapor entrance area constant, i.e. the anode open ratio is reduced. By this strategy, the VF-MFC can achieve 48% higher power output and elevated fuel utilization from 27.5% to 41.8%, when an anode open ratio of 1:3 is adopted.

Key words:

Vapor-feed, microfluidic fuel cell, numerical modeling, fuel boundary layer, fuel utilization

Nomenclature:

Symbols

ρ : Density (kg m^{-3})

u : Velocity (m s^{-1})

P : Pressure (Pa)

μ : Dynamic viscosity ($\text{Pa}\cdot\text{s}$)

ω : Mass fraction

j : Diffusion flux ($\text{kg m}^{-2} \text{s}^{-1}$)

S : Production/consumption rate due to electrochemical reactions ($\text{kg m}^{-3} \text{s}^{-1}$)

M : Molar mass (kg mol^{-1})

D : Diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)

c : Molar concentration (mol m^{-3})

k : Diffusion resistance coefficient

ϵ : Porosity of GDL

M_n : Average molar mass of the mixture (kg mol^{-1})

σ : Conductivity (S m^{-1})

φ : Potential (V)

i : Current density (A m^{-2})

v : Stoichiometric coefficient

n : Number of transferred electrons

F : Faraday's constant (96485 C mol^{-1})

i_0 : Exchange current density (A m^{-2})

χ : Reaction order

α : Charge transfer coefficient

1
2
3
4 η : Activation overpotential (V)
5

6
7 R: Gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)
8

9 T: Temperature (K)
10

11 E_{eq} : Equilibrium potential (V)
12

13
14 Q: Charge source term (A m^{-3})
15
16
17
18

19 *Subscript:*
20

21 a: Anode
22

23
24 c: Cathode
25

26 f: fuel
27

28
29 i, j, k: Species
30

31 l: Electrolyte
32

33
34 o: oxidant
35

36 s: Electrode
37

38
39 ϕ_0 : Standard, reference, or boundary value
40

41 eff: effective
42
43
44

45 **1. Introduction**

46
47

48 Microfluidic fuel cell (MFC) is a novel type of fuel cell, which does not need a
49 physical membrane to separate its two electrodes and the corresponding reactants [1, 2].
50
51 Instead, MFC generally employs two laminar streams, one dissolved with the fuel (i.e. the
52 anolyte) and the other dissolved with the oxidant (i.e. the catholyte), flowing directly into
53
54 its microfluidic channel and passing between its two electrodes, as shown in Fig. 1(a).
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4 Benefited from the low Reynolds number of the microfluidic flow, the vigorous
5
6 convective mixing is eliminated, with only a slow diffusion process occurring at the
7
8 anolyte-catholyte interface. In this manner, the fuel and oxidant are naturally separated to
9
10 maintain a successful fuel cell operation.
11
12
13

14 Attributed to their simpler structure, MFCs possess many advantages compared with
15
16 the conventional membrane-based fuel cells such as the proton-exchange membrane fuel
17
18 cell (PEMFC). First of all, the cell cost is significantly reduced due to the elimination of
19
20 the costly membrane. In addition, all the membrane-related issues can be avoided
21
22 including membrane dehydration and degradation, and its sensitivity to reaction
23
24 environment. Moreover, the choice of fuel, oxidant, and electrolyte species is greatly
25
26 extended in MFCs, among which the dual-electrolyte configuration with acid
27
28 environment on the cathode side and alkaline environment on the anode side has been
29
30 demonstrated to be powerful for boosting up the power output [3-5]. Furthermore, water
31
32 and heat management is inherently fulfilled by the continuous microfluidic flow, leading
33
34 to a greatly simplified fuel cell system. Nevertheless, the current MFC technology still
35
36 faces many unsolved problems which have greatly impeded their further development
37
38 and practical application. First, the employment of bulk aqueous solution would
39
40 dramatically lower down the system energy density. In addition, the strict requirement on
41
42 electrolyte flow rate control would require complex ancillary components such as micro-
43
44 pumps and a stable working environment, which greatly restricts their application
45
46 prospect. Furthermore, the fuel utilization is generally low since the dissolved fuel needs
47
48 to diffuse to the anode catalyst layer (CL) from the bulk anolyte, which is a very slow
49
50 process compared with the convective transport along the microfluidic channel.
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Consequently, a large portion of the fuel has no chance to be reacted, leading to low fuel utilization of less than 10% [6]. To tackle this issue, lower electrolyte flow rates are generally adopted, which, however, can degrade the cell performance by two aspects. The fuel depletion effect would be intensified on the anode side while the fuel crossover effect would be aggravated on the cathode side. As a consequence, the fuel utilization is improved at the price of sacrificed cell performance and even catalyst poisoning. This dilemma between cell performance and fuel utilization should also be solved for future MFC development.

Previously we have developed a vapor-feed MFC (VF-MFC) which has a totally different fuel delivery mode compared with the conventional liquid-feed MFC (LF-MFC) [6]. As shown in Fig. 1(b), instead of dissolving the fuel into the anolyte and feeding it to the anode from inside the channel, the VF-MFC utilizes fuel vapor from outside the channel which diffuses through the porous anode and dissolves into the flowing electrolyte. In this manner, bulk anolyte wastage is avoided, which leads to a more economic fuel delivery pattern and, consequently, a higher fuel utilization in the order of 40%. In addition, the cell performance of VF-MFC was not sacrificed. Our experimental study has already proved the advantage of VF-MFC. However, the specific mechanism behind its superiority is not clearly understood yet, which is either difficult or expensive to be explored experimentally.

Numerical modeling is a convenient and economical method for MFC research and development, which can not only reveal the deep-going mechanisms behind the experimental phenomenon but also comprehensively optimize the cell structure and operation parameters. Great efforts have been made on MFC modeling over the past

decade, including the investigation of fuel utilization optimization [7-17], fuel crossover suppression [18-20], air-breathing cathode [21-23], flow-through electrodes [24-27], and other related systematic issues [28-30]. In spite of all these achievements, the current MFC modeling is mostly focused on conventional LF-MFC. To the best of our knowledge, no modeling study has ever been conducted on VF-MFC yet because this is a newly emerged technology. Therefore, in this work we have developed a 3D isothermal VF-MFC model using a finite element method (FEM) software, Comsol® 4.2. First, in order to ensure the reliability of the proposed model the simulation results under different test conditions have been validated by the previous experimental data. Next, the species distribution inside the electrolyte during cell operation has been thoroughly investigated to reveal the mechanism behind the superiority of VF-MFC. Furthermore, several cell structural and operational parameters, including the electrolyte flow rate, the fuel evaporation area and the electrode open ratio, have been studied, respectively, in order to optimize the performance of VF-MFCs.

2. Numerical model

2.1 Computational domain

The present model is based on a vertical VF-MFC configuration with a fuel-breathing anode and an air-breathing cathode, which has identical structural parameters with our previous experimental prototype [6]. As shown in Fig. 2, the computational domain includes a vapor chamber (2) whose bottom is set as the fuel evaporation surface (1), an anode (3) on the front face of the vapor chamber, a cathode (7) opposite to the anode, and an electrolyte flow (5) between the two electrodes. In addition, two grooves (4 and 6) are

added between anode-electrolyte and cathode-electrolyte, respectively, to more realistically mimic the cell structure of our previous experimental prototype [6]. Neat methanol is chosen as the vapor source and 1M potassium hydroxide (KOH) solution is used as the electrolyte.

On the cathode side, the oxygen concentration gradient through the thin gas diffusion layer (GDL) is assumed to be negligible according to Shaegh. et al. [10] Therefore, the concentration of dissolved oxygen at the cathode CL is set to be at saturated level (0.25 mol m⁻³) all the time [31]. As for the anode side, methanol vapor from the vapor chamber will continuously diffuse through the porous anode GDL and dissolve into the electrolyte at the anode CL, where the methanol oxidation reaction (MOR) takes place:

The generated electrons will flow through an external circuit to the cathode side, where oxygen reduction reaction (ORR) takes place:

In order to simplify the computation, both of the anode and cathode CLs are treated as 2D surfaces, which is reasonable considering the negligible thickness of CL in real case (~20 μm) [32].

2.2 Governing equations

2.2.1 Hydrodynamics

Due to the small cell dimension, the Reynolds number of the electrolyte flow in the present study is calculated to be 0.28 at a typical flow rate of $50 \mu\text{l min}^{-1}$, that is, a laminar flow. This laminar flow in the micro-channel is governed by the continuity equation (Eqn. 3) and Navier-Stokes equation (Eqn. 4):

$$\nabla \cdot (\rho \mathbf{u}) = 0 \quad (3)$$

$$\rho(\mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + \nabla \cdot (\mu(\nabla \mathbf{u})) \quad (4)$$

As for the vapor chamber, the bulk motion of the methanol vapor is negligible since the cell is kept static. Therefore, only diffusion is considered inside.

2.2.2 Mass transport

Species transport inside the vapor chamber, porous anode and flowing electrolyte is generally governed by the species conservation equation (Eqn. 5):

$$\nabla \cdot (\rho \omega_i \mathbf{u}) = -\nabla \cdot \mathbf{j}_i + S_i \quad (5)$$

In the vapor chamber, the diffusion of methanol vapor is described by Fick's law (Eqn. 6), which is reasonable due to its low concentration in air. As the present model is a steady-state model which only studies the initial cell performance of VF-MFC, the dilution effect of water vapor on the methanol fuel is not considered in this domain for

simplicity. Besides, since both the concentration of methanol vapor and water vapor in air are very low, the effect on their diffusion coefficient from each other is considered to be negligible. Moreover, Fig. S1 in the supplementary material shows the cell performance from the model with and without the effect of water vapor transport, which indicates negligible difference between them. Therefore, water vapor is not considered in the present model.

$$j = -M \cdot D \nabla c \quad (6)$$

In the anode GDL, Fick's law is also applicable to methanol vapor (Eqn. 7) but an effective diffusion coefficient should be adopted instead of the bulk diffusion coefficient according to Bruggeman correction (Eqn. 8). In addition, a highly hydrophobic anode GDL is adopted in our previous experiment, which is a carbon paper covered by a thick PTFE coating as shown in Fig. 2. To include the hindering effect of this PTFE coating on the delivery of methanol vapor, a diffusion resistance coefficient, k , is also introduced here.

$$j = -k \cdot M \cdot D_{eff} \nabla c \quad (7)$$

$$D_{eff} = \varepsilon^{1.5} D \quad (8)$$

At the anode CL, the flux of methanol vapor is assumed to be totally dissolved into the flowing electrolyte before the electro-oxidation reaction (Eqn. 9). This assumption is also

reasonable since MOR can only occur at the triple-phase boundary (TPB) where methanol vapor, catalyst particle and aqueous electrolyte meet together, while methanol vapor can easily dissolve into the aqueous electrolyte.

$$j_{vapor,at\ CL} = j_{dissolved,at\ CL} \quad (9)$$

As for the flowing electrolyte, Maxwell–Stefan theory with a mixture-average approximation is utilized to describe the diffusion process of multiple components in water, including methanol, oxygen and KOH.

$$j_i = -(\rho D_i \nabla \omega_i + \rho \omega_i D_i \frac{\nabla M_n}{M_n}) \quad (10)$$

$$D_i = \frac{1-\omega_i}{\sum_{k \neq i} \frac{x_k}{D_{ik}}} \quad (11)$$

$$M_n = (\sum_i \frac{\omega_i}{M_i})^{-1} \quad (12)$$

Maxwell–Stefan diffusivities are calculated by the generalized Vignes equation [33]:

$$D_{ij} = (D_{ij}^{x_i \rightarrow 1})^{x_i} (D_{ij}^{x_j \rightarrow 1})^{x_j} \prod_{k=1, k \neq i, j}^n (D_{ij}^{x_k \rightarrow 1})^{x_k} \quad (13)$$

where “ $D_{ij}^{x_j \rightarrow 1}$,” represents the diffusivity of species “i” in species “j” at infinite dilution,

which can be calculated by the following Wilke-Chang Equation [34]:

$$D = 7.4 \times 10^{-8} \frac{\sqrt{xM} * T}{\mu V^{0.8}} \quad (14)$$

where x is the association parameter, M is the molar mass of solvent, T is the temperature, μ is the viscosity of solution, and V is the molar volume of solute.

2.2.3 Electrochemical kinetics

Electrolyte potential is derived from the conservation equation of charge:

$$-\sigma \nabla \varphi = i \quad (15)$$

The species consumption or production rates due to electrochemical reactions are derived from:

$$S_i = M_i \frac{v_i \nabla \cdot i}{n_i F} \quad (16)$$

The current density is calculated by the Butler-Volmer equation (Eqn. 17), while the effect of fuel crossover is not considered in the present model because the concentration of crossovered fuel is found to be negligible at the cathode CL.

$$i = i_0 \prod_i \left(\frac{c_i}{c_{i,0}} \right)^{\chi} \left(\exp \left(\frac{\alpha_a F \eta}{RT} \right) - \exp \left(\frac{-\alpha_c F \eta}{RT} \right) \right) \quad (17)$$

$$\eta = \varphi_s - \varphi_l - E_{eq} \quad (18)$$

At the electrode surfaces, current source Q is derived from:

$$Q = \nabla \cdot i \quad (19)$$

2.3 Boundary conditions

For the hydrodynamics, velocity at the channel inlet and pressure at the channel outlet are respectively set as follows:

$$u_{inlet} = u_0 \quad (20)$$

$$P_{outlet} = 0 \quad (21)$$

In addition, non-slip condition is applied to the channel boundaries, where the velocity is set to be zero.

For the mass transport in the vapor chamber and porous anode, methanol vapor concentration at the fuel evaporation surface is set to be the value of saturated vapor concentration (6.8 mol m^{-3} for neat methanol at 25°C [35]), while the vapor concentration at the anode CL is set to be zero considering the unlimited solubility of methanol in water. As for the mass transport in the electrolyte, KOH concentration is set at the flow inlet and convective mass transport is set at the flow outlet. To simplify the cathode calculation, oxygen concentration at the cathode CL is set to be constant as mentioned in Section 2.1.

This assumption is further validated as shown in Fig. S2 in the supplementary material.

For the calculation of current distribution, potentials of the anode and cathode outer surfaces are set to be ground and cell voltage, respectively.

Key input parameters used in this study are summarized in Table-1. The polarization curve of the experimental benchmark case (i.e. neat methanol as fuel, 1M KOH as electrolyte, at 50 $\mu\text{l min}^{-1}$) is utilized to fit the $i_{0,a}$, $i_{0,c}$ and k .

Table-1 Key input parameters in the present VF-MFC model

Parameters	Values	References
C_o	0.25 mol m^{-3}	[19]
$C_{0,o}$	1.25 mol m^{-3}	[19]
$C_{0,f}$	0.1 mol L^{-1}	[36]
$i_{0,a}$	0.025 A m^{-2}	Fitted
$i_{0,c}$	3 A m^{-2}	Fitted
T	298.15 K	-
χ	1	[37]
α_a	0.52	[36]
α_c	0.5	[19]
σ_l	0.2153, 0.3778, 0.494 S cm^{-1} (for 1, 2, 3 M KOH)	[38]
σ_s	381.8 S m^{-1}	From the manufacturer
$E_{eq,a}$	-0.81 V	-
$E_{eq,c}$	0.4 V	-
k	0.1	Fitted
ϵ	0.7	[27]
$D_{f,vapor}$	$0.15 \text{ cm}^2 \text{ s}^{-1}$	[39]
$C_{f,vapor}$ (At the evaporation surface)	2.1, 3.1, 4.6, 6.8 mol m^{-3} (for 10M, 15M, 20M and neat methanol fuel)	[40]

2.4 Numerical solution

A commercial software, COMSOL Multiphysics 4.2, is employed for the present study. After developing the VF-MFC model, a free tetrahedral mesh was utilized to discretize the computational domain, with larger elements for the vapor chamber and much smaller

elements for the electrodes, electrode grooves and the microfluidic channel. To ensure the accuracy of the modelling results, grid independence check has been conducted first by gradually refining the mesh from 48287 to 370933 elements. The corresponding element size (minimum) was decreased from 57.7 to 2.9 μm , and the corresponding computational time was increased from 16 minutes to 1 hour. The simulated polarization curves under different grid densities were quite identical with each other, with the highest relative difference of only 0.7% between the 48287-element mesh and the 370933-element mesh. Therefore, the mesh with 48287 elements was regarded to be both accurate and economical for the subsequent studies. To obtain the polarization curves, a parametric sweep solver based on cell voltage is utilized to calculate the current densities from 0.9 V to 0 V with an interval of 0.05 V. The stationary segregated multifrontal massively parallel solver (MUMPS) is used for the calculation process.

3. Results and discussion

3.1 Model validation

Before using the present model for specific studies, reliability of its results was validated by comparing with the experimental data of our previous [6] and present studies. It is worth mentioning that experimental results of the 10, 15 and 20 M methanol cases in the previous study are all replaced by updated data in the present study, since they were slightly over-estimated in our previous work. This is because that in the previous work, after testing of the benchmark case (i.e. neat methanol as fuel), the same cell was repeatedly utilized to test the different fuel concentrations from 10 to 20 M. As a consequence, the residual of dissolved methanol inside the porous anode CL after the neat

methanol test might have caused positive bias to the cell performance with lower fuel concentrations, especially for the 10 M case. Therefore, in this study, new cells have been employed to re-test the 10, 15 and 20 M cases, which should be more reliable for the present model validation. Fig. 3 presents the validation results under various test conditions, including different fuel and electrolyte concentrations, and different electrolyte flow rates. As shown in the figure, the modeling results generally fit the experimental data very well, and the relative difference at all data points are within $\pm 10\%$. In Fig. 3(a), the characteristic of mass transfer resistance at lower cell voltages when using lower concentrations of methanol as vapor source can be well-simulated by the present model. In addition, Fig. 3(b) shows that when higher electrolyte concentrations were applied, the decreased cell ohmic resistance can also be revealed by the present model. Furthermore, it was previously found that the VF-MFC performance is insensitive to the electrolyte flow rate [6], which is the same case for the modeling results as shown in Fig. 3(c). It is also worth mentioning that the deviation between the experiment and the simulation is relatively high at the high current density region (but still within $\pm 10\%$) compared with other data points. Nevertheless, considering the fact that the experimental results here are actually averaged values with error bars (not shown in the figure) obtained from multiple tests, this deviation is considered to be acceptable. In conclusion, the present model is found to be sufficiently reliable to simulate the VF-MFC operation, which will be utilized to study the deep-going mechanisms behind its special features and to do further optimizations to its performance in the following sections.

3.2 Fuel distribution in the VF-MFC

In order to better illustrate the advantages of the VF-MFC, a LF-MFC model was also developed in this section for comparison purpose as shown in Fig. 4(a), which has identical input parameters with the VF-MFC model (See Table-1). Grid independence check has also been conducted for this model, and a mesh with 106560 elements was found to be accurate and suitable. The major difference between them lies on the anode side, where dissolved fuel in the anolyte was employed to provide fuel to the anode CL from inside the channel, instead of providing fuel vapor from outside the channel. Here it is worth mentioning that even though the methanol vapor can diffuse throughout the whole anode of the vapor-feed cell, it can only get oxidized at the thin catalyst layer on one side of the anode; while in the liquid-feed cell, the dissolved methanol from anolyte is also oxidized at this thin catalyst layer. Therefore, it is fair to compare the performance of the two different cells, since they utilize the same anode material which has identical electro-catalytic surface area. Fig. 4(b) compares the VF-MFC performance tested by neat methanol with the LF-MFC performances tested by 0.1-1 M methanol solution, which shows that the polarization curve of the VF-MFC is similar to the LF-MFC with 0.5 M MeOH as fuel. This similarity between their performances can be explained by the average fuel concentration at the anode CL of the VF-MFC, which is 0.59 M and close to 0.5 M of the LF-MFC case. The above results indicate that the vapor-feed mode can supply enough amount of fuel to the anode side to achieve comparable power output with conventional liquid-feed MFCs. However, as shown in Fig. 4(c), the VF-MFC achieves much higher fuel utilization (27.5%) than the LF-MFC with 0.5 M methanol as fuel (3.7%). In other words, the VF-MFC can achieve both high cell performance and high fuel utilization at the same time, while the LF-MFC suffers from the inevitable trade-off

1
2
3
4 between power output and fuel efficiency. To increase the fuel utilization of LF-MFC,
5
6 even though a much diluted anolyte (0.1 M) is employed instead, the fuel utilization is
7
8 still much lower (7.3%) than that of the VF-MFC, not to mention the greatly sacrificed
9
10 cell performance as shown in Fig. 4(b).
11
12
13

14 To figure out the specific reason behind the superior performance of VF-MFC, the
15
16 distribution of fuel inside its microfluidic channel is illustrated in Fig. 5(a). As shown by
17
18 the cross-sectional view of the channel, the dissolved methanol mainly locates in a thin
19
20 layer nearby the anode CL, with higher fuel concentration locates at the two corners of
21
22 the anode groove. As for the whole anode surface, a higher fuel concentration generally
23
24 locates at its four sides, while a lower fuel concentration generally locates in the middle.
25
26 This feature can be explained by the different local flow rates of electrolyte at different
27
28 locations nearby the anode. As shown in the left inset of Fig. 5(a), the local flow rates at
29
30 the four sides of the anode groove are dragged down by a stronger boundary layer effect,
31
32 so less amount of dissolved fuel is removed by the convective electrolyte flow. As for the
33
34 middle part of the anode groove, the local flow rates would be higher, leading to a faster
35
36 removal of the dissolved fuel. This controlled fuel boundary layer in the VF-MFC can not
37
38 only support the anode oxidation reaction sufficiently, but also greatly alleviate the
39
40 wastage of fuel. As a consequence, both satisfactory cell performance and high fuel
41
42 utilization can be realized at the same time.
43
44
45
46
47
48
49

50 For comparison purpose, the distribution of fuel in the LF-MFC is also presented in Fig.
51
52 5(b), which shows that the left half of the channel is full of dissolved fuel. Therefore, it is
53
54 very straightforward that the VF-MFC has a more efficient fuel delivery pattern, while
55
56 the LF-MFC would waste most of its fuel by convective electrolyte flow.
57
58
59
60
61
62
63
64
65

3.3 Parametric study and optimization

3.3.1 Effect of electrolyte flow rate

In section 3.2, it is found that the VF-MFC performance is rather insensitive to the electrolyte flow rate, behind which possible mechanisms will be further investigated in this section. As shown in Fig. 6(a), the polarization curve of VF-MFC can still maintain a relatively stable feature even with a very high electrolyte flow rate of $1000 \mu\text{l min}^{-1}$. In general, when the electrolyte flow rate increases, the initial cell performance at higher cell voltages will slightly decrease, while the current density at lower voltages will slightly increase. This phenomenon can be explained by the mass transfer resistance from the methanol fuel as well as the hydroxyl ions, both of which participate in the anode reaction.

As shown in Fig. 6(b), when the electrolyte flow rate rises up, the fuel concentration at the anode CL at OCV gradually drops from 3.1 M at $1 \mu\text{l min}^{-1}$ to 0.21 M at $1000 \mu\text{l min}^{-1}$, while the concentration of the crossover fuel at the cathode CL dramatically decreases from 1.7 M at $1 \mu\text{l min}^{-1}$ to less than 1 mM after reaching $50 \mu\text{l min}^{-1}$. This special feature of VF-MFC can not only retain a relatively sufficient fuel concentration on the anode side but also effectively suppress the fuel crossover on the cathode side. Consequently, the initial cell performance at higher voltages would only slightly drop at higher flow rates. This is attributed to the boundary layer effect, which leads to a very small flow rate and, therefore, a low removal rate of dissolved methanol nearby the anode surface. Consequently, the fuel concentration can still maintain 0.21 M even at $1000 \mu\text{l min}^{-1}$. As for the cathode side, since the electrolyte flow rate in the middle of the channel is less

1
2
3
4 affected by the channel boundaries, the crossovered fuel can be effectively removed away
5
6 when the flow rate increases.
7

8
9 Fig. 6(c) reveals that the short-circuit current density of the VF-MFC will dramatically
10 increase when the electrolyte flow rate elevates from 10 to 400 $\mu\text{l min}^{-1}$, and then slightly
11 decrease after 400 $\mu\text{l min}^{-1}$. This can be explained by variations of both the fuel
12 concentration and the hydroxyl ion concentration at the anode CL. When the flow rate is
13 as low as 10 $\mu\text{l min}^{-1}$, the fuel concentration is sufficiently high but the hydroxyl ion
14 concentration is close to zero, indicating a significant hydroxyl transfer resistance due to
15 the slow electrolyte replenishment nearby the anode. As the flow rate gradually rises to
16 400 $\mu\text{l min}^{-1}$, this hydroxyl transfer resistance is greatly alleviated, leading to a peak
17 short-circuit current density of 224.6 mA cm^{-2} . At the same time, the fuel concentration is
18 still sufficient (0.3 M) to support the anode reaction. However, when the flow rate further
19 increases to 1000 $\mu\text{l min}^{-1}$, the short-circuit current density will be slightly dragged down
20 to 223.5 mA cm^{-2} by the decreasing fuel concentration.
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37

38 Fig. 6(d) exhibits the relationship between fuel utilization at the peak power point (0.3
39 V) and the electrolyte flow rate. The fuel utilization is calculated by dividing the
40 generated charge quantity to the input fuel:
41
42
43
44
45
46
47

$$\xi = \frac{i}{nFN} \quad (22)$$

48
49
50
51
52
53 where i is the current density (A m^{-2}), n is the number of transferred electrons (6 for
54 methanol), F is the Faraday's constant (96485 C mol^{-1}), and N is the input flux of fuel
55 from the vapor chamber into the anode ($\text{mol m}^{-2} \text{ s}^{-1}$). As shown in the figure, the fuel
56
57
58
59
60
61
62
63
64
65

utilization keeps decreasing with increasing electrolyte flow rate, from 27.5% at 50 $\mu\text{l min}^{-1}$ to 23% at 1000 $\mu\text{l min}^{-1}$. This is because that a faster flow of electrolyte will carry the dissolved fuel away from the anode CL more promptly, leading to a higher loss rate of fuel. This is also reflected by the decreased fuel concentration at the anode CL as indicated in Fig. 6(b). Nevertheless, the decrease ratio of fuel utilization is only 16.4% for the VF-MFC when the electrolyte flow rate is increased by 20 times, while the corresponding value for the LF-MFC is as high as 93.8%. This indicates that the fuel utilization of VF-MFC is also relatively insensitive to its electrolyte flow rate, which is favored in practical applications where a precise control of flow rate is either impractical or high-cost.

3.3.2 Effect of fuel evaporation area

In a VF-MFC, the fuel evaporation area (i.e. the surface area of stored fuel) is very important to the supply of fuel vapor, which should be correlated with the electrode reaction area. A lower evaporation-reaction area ratio may lead to insufficient fuel supply, while a higher ratio may lead to unnecessary fuel wastage. Fig. 7(a) exhibits the distribution of vapor concentration inside the vapor chamber. The average vapor concentration is 3.0, 5.1, 5.9, and 6.1 mM with the evaporation area of 1, 25, 100, and 225 mm^2 , respectively, while the saturated vapor concentration at vicinity of the neat methanol surface is 6.8 mM. This implies that an evaporation area of 100 mm^2 might be sufficient for the present case with an anode area of 9 mm^2 . Fig. 7(b) further proves this conclusion, in which the 1 mm^2 case encounters an evident mass transport resistance at lower cell voltages, while the cell performance reaches a plateau when the fuel

1
2
3
4 evaporation area rises to 100 mm². Therefore, an evaporation-reaction area ratio of 11.1 is
5
6 sufficient for the present case. It is also worth mentioning that this value may change with
7
8 the variation of cell parameters, such as the anode catalyst loading.
9

10
11 Effect of the evaporation area on fuel utilization is also studied as shown in Fig. 7(c).
12
13 With a smaller fuel evaporation area of 1 mm², the dissolved fuel can be better utilized by
14
15 the anode CL, achieving a higher fuel utilization of 40.5%. When the evaporation area
16
17 increases by 100 times, the fuel utilization will drop to 27.7% due to the faster supply of
18
19 fuel vapor into the anode. In conclusion, an extra cell component for adjusting fuel
20
21 evaporation area could be added to the present VF-MFC, in order to meet requirements
22
23 from different mission profiles.
24
25
26
27
28
29
30

31 **3.3.3 Effect of anode open ratio**

32
33 As mentioned in Section 3.3.1, the extent of fuel crossover is greatly alleviated in the
34
35 VF-MFC. Therefore, it is feasible to extend the electrode length towards the channel
36
37 outlet while maintaining the vapor entrance area as shown in Fig. 8(a), which may better
38
39 utilize the dissolved methanol in electrolyte thus further improve the fuel utilization. To
40
41 quantify this effect, a parameter called anode open ratio is employed, which is defined as
42
43 the ratio between the vapor entrance area and the electrode catalytic area. As shown in
44
45 Fig. 8(a), five different anode open ratios were investigated ranging from 1.0:1.0 to
46
47 1.0:3.0. The fuel concentration at the extended part of the anode CL is much lower than
48
49 that at the original part, which is due to the continuous diffusion loss into the flowing
50
51 electrolyte. Nevertheless, the absolute current and power output can be improved by this
52
53 strategy, with the peak power increased by 48% from 2.7 to 4.0 mW as shown in Fig. 8(b).
54
55
56
57
58
59
60
61
62
63
64
65

Furthermore, Fig. 8(c) shows that the fuel utilization is improved from 28% to 42% when the electrode length is increased by 3 times. This outcome is straightforward since the extended electrode area can further consume the dissolved fuel inside the electrolyte. In addition, the decreased fuel concentration at the outlet also proves the same conclusion.

Even though it is beneficial to both the power output and the fuel utilization of VF-MFC, there are still several issues related to this fuel cell design. First, with the extension of the electrode length, the extent of fuel crossover will be aggravated especially at the farther part of the cathode. As shown in Fig. 8(d), the average fuel concentration at the cathode CL is increased from 0.6 to 2.9 mM when the electrode length is extended by 3 times, which is still relatively negligible. However, further extension of the electrode length may cause severe crossover problem, which calls for methanol-tolerant ORR catalysts instead of the present Pt/C catalyst. In addition to the aggravated fuel crossover, the extension of electrode length will also bring a higher system cost, since electrodes are the most expensive component in the MFC. Therefore, non-noble catalysts should be applied to the extended part of the electrode instead of the present Pt-Ru catalyst.

4. Conclusion

VF-MFC possesses distinctive advantages against the conventional LF-MFC, such as the decoupled power output with fuel utilization, insensitive cell performance to electrolyte flow rate, alleviated fuel crossover, and so on. To further explore the mechanisms behind these specific features of VF-MFC, a numerical model has been built for the first time in this work. The simulated polarization curves under various testing conditions, including different fuel and electrolyte concentrations, and different

electrolyte flow rates, fit the experimental results quite well, indicating the reliability of the proposed model. By investigating the species transport and distribution inside the micro-channel, it is found that the dissolved fuel is mainly located in a controlled boundary layer nearby the anode catalytic surface, while the rest of the channel part is almost free from the fuel. In this manner, the supply of the fuel in a VF-MFC is economically controlled compared with the severe wastage of fuel in a LF-MFC, leading to much improved fuel utilization. To further optimize the VF-MFC performance, effects of electrolyte flow rate, fuel evaporation area, and anode open ratio were also investigated. Both the cell performance and the fuel utilization are found to be relatively insensitive to the electrolyte flow rate, which can be probably attributed to the boundary layer effect that helps to reserve the fuel from convective loss. A fuel evaporation area of 100 mm^2 is sufficient for the present VF-MFC with an electrode area of 9 mm^2 , which corresponds to an evaporation-reaction area ratio of 11:1. Finally, by extending the electrode length by three times while maintaining the vapor entrance area, the fuel utilization could be further improved from 27.5% to 41.8%. This method is especially suitable for VF-MFC when inexpensive non-noble catalysts are employed instead of the current Pt-based catalyst.

Acknowledgement

This project is funded by the Hong Kong Research Grant Council GRF#714313.

References:

- [1] E. Kjeang, N. Djilali, D. Sinton, Microfluidic fuel cells: A review, *Journal of Power Sources*, 186 (2009) 353-369.
- [2] S.A.M. Shaegh, N.-T. Nguyen, S.H. Chan, A review on membraneless laminar flow-based fuel cells, *International Journal of Hydrogen Energy*, 36 (2011) 5675-5694.
- [3] J.L. Cohen, D.J. Volpe, D.A. Westly, A. Pechenik, H.D. Abruña, A Dual Electrolyte H₂/O₂ Planar Membraneless Microchannel Fuel Cell System with Open Circuit Potentials in Excess of 1.4 V, *Langmuir*, 21 (2005) 3544-3550.
- [4] X. Lu, J. Xuan, D.Y. Leung, H. Zou, J. Li, H. Wang, H. Wang, A switchable pH-differential unitized regenerative fuel cell with high performance, *Journal of Power Sources*, 314 (2016) 76-84.
- [5] B. Chen, D.Y. Leung, J. Xuan, H. Wang, A mixed-pH dual-electrolyte microfluidic aluminum–air cell with high performance, *Applied Energy*, (2015).
- [6] Y. Wang, D.Y. Leung, J. Xuan, H. Wang, A vapor feed methanol microfluidic fuel cell with high fuel and energy efficiency, *Applied Energy*, 147 (2015) 456-465.
- [7] A. Bazylak, D. Sinton, N. Djilali, Improved fuel utilization in microfluidic fuel cells: A computational study, *Journal of Power Sources*, 143 (2005) 57-66.
- [8] M.-H. Chang, F. Chen, N.-S. Fang, Analysis of membraneless fuel cell using laminar flow in a Y-shaped microchannel, *Journal of Power Sources*, 159 (2006) 810-816.
- [9] J. Phirani, S. Basu, Analyses of fuel utilization in microfluidic fuel cell, *Journal of Power Sources*, 175 (2008) 261-265.
- [10] S.A.M. Shaegh, N.-T. Nguyen, S.H. Chan, An air-breathing microfluidic formic acid fuel cell with a porous planar anode: experimental and numerical investigations, *Journal of Micromechanics and Microengineering*, 20 (2010) 105008.
- [11] J. Lee, K.G. Lim, G.T.R. Palmore, A. Tripathi, Optimization of microfluidic fuel cells using transport principles, *Analytical chemistry*, 79 (2007) 7301-7307.
- [12] D.H. Ahmed, H.B. Park, H.J. Sung, Optimum geometrical design for improved fuel utilization in membraneless micro fuel cell, *Journal of Power Sources*, 185 (2008) 143-152.
- [13] J. Xuan, M.K.H. Leung, D.Y.C. Leung, M. Ni, H. Wang, Hydrodynamic focusing in microfluidic membraneless fuel cells: Breaking the trade-off between fuel utilization and

- current density, *International Journal of Hydrogen Energy*, 36 (2011) 11075-11084.
- [14] A.E. Khabbazi, A. Richards, M. Hoorfar, Numerical study of the effect of the channel and electrode geometry on the performance of microfluidic fuel cells, *Journal of Power Sources*, 195 (2010) 8141-8151.
- [15] R.A. García-Cuevas, I. Cervantes, L.G. Arriaga, I.A. Diaz-Diaz, Toward geometrical design improvement of membraneless fuel cells: Numerical study, *International Journal of Hydrogen Energy*, 38 (2013) 14791-14800.
- [16] J. Xuan, D.Y. Leung, M.K. Leung, H. Wang, M. Ni, Chaotic flow-based fuel cell built on counter-flow microfluidic network: Predicting the over-limiting current behavior, *Journal of Power Sources*, 196 (2011) 9391-9397.
- [17] H. Xu, H. Zhang, H. Wang, D.Y. Leung, L. Zhang, J. Cao, K. Jiao, J. Xuan, Counter-flow formic acid microfluidic fuel cell with high fuel utilization exceeding 90%, *Applied Energy*, 160 (2015) 930-936.
- [18] J. Xuan, M.K.H. Leung, D.Y.C. Leung, H. Wang, Laminar flow-based fuel cell working under critical conditions: The effect of parasitic current, *Applied Energy*, 90 (2012) 87-93.
- [19] H. Zhang, J. Xuan, H. Xu, M.K.H. Leung, D.Y.C. Leung, L. Zhang, H. Wang, L. Wang, Enabling high-concentrated fuel operation of fuel cells with microfluidic principles: A feasibility study, *Applied Energy*, 112 (2013) 1131-1137.
- [20] H.B. Park, D.H. Ahmed, K.H. Lee, H.J. Sung, An H-shaped design for membraneless micro fuel cells, *Electrochimica Acta*, 54 (2009) 4416-4425.
- [21] J. Xuan, D.Y.C. Leung, H. Wang, M.K.H. Leung, B. Wang, M. Ni, Air-breathing membraneless laminar flow-based fuel cells: Do they breathe enough oxygen?, *Applied Energy*, 104 (2013) 400-407.
- [22] H. Wang, D.Y.C. Leung, J. Xuan, Modeling of an air cathode for microfluidic fuel cells: Transport and polarization behaviors, *International Journal of Hydrogen Energy*, 36 (2011) 14704-14718.
- [23] M. Moein-Jahromi, S. Movahed, M. Kermani, Numerical study of the cathode electrode in the Microfluidic Fuel Cell using agglomerate model, *Journal of Power Sources*, 277 (2015) 180-192.
- [24] D. Krishnamurthy, E.O. Johansson, J.W. Lee, E. Kjeang, Computational modeling of

microfluidic fuel cells with flow-through porous electrodes, *Journal of Power Sources*, 196 (2011) 10019-10031.

[25] L. Li, K. Zheng, M. Ni, M.K. Leung, J. Xuan, Partial modification of flow-through porous electrodes in microfluidic fuel cell, *Energy*, 88 (2015) 563-571.

[26] L. Li, W. Fan, J. Xuan, M.K. Leung, Dimensionless parametric sensitivity analysis of microfluidic fuel cell with flow-through porous electrodes, *Electrochimica Acta*, 187 (2016) 636-645.

[27] B. Zhang, D.-d. Ye, P.-C. Sui, N. Djilali, X. Zhu, Computational modeling of air-breathing microfluidic fuel cells with flow-over and flow-through anodes, *Journal of Power Sources*, 259 (2014) 15-24.

[28] J. Xuan, M.K.H. Leung, D.Y.C. Leung, M. Ni, Density-induced asymmetric pair of Dean vortices and its effects on mass transfer in a curved microchannel with two-layer laminar stream, *Chemical Engineering Journal*, 171 (2011) 216-223.

[29] J. Xuan, M.K.H. Leung, D.Y.C. Leung, H. Wang, Towards orientation-independent performance of membraneless microfluidic fuel cell: Understanding the gravity effects, *Applied Energy*, 90 (2012) 80-86.

[30] H. Zhang, M.K.H. Leung, J. Xuan, H. Xu, L. Zhang, D.Y.C. Leung, H. Wang, Energy and exergy analysis of microfluidic fuel cell, *International Journal of Hydrogen Energy*, 38 (2013) 6526-6536.

[31] F. Chen, M.-H. Chang, M.-K. Lin, Analysis of membraneless formic acid microfuel cell using a planar microchannel, *Electrochimica acta*, 52 (2007) 2506-2514.

[32] H. Deng, J. Chen, K. Jiao, X. Huang, An analytical model for alkaline membrane direct methanol fuel cell, *International Journal of Heat and Mass Transfer*, 74 (2014) 376-390.

[33] X. Liu, T.J. Vlugt, A. Bardow, Predictive Darken equation for Maxwell-Stefan diffusivities in multicomponent mixtures, *Industrial & Engineering Chemistry Research*, 50 (2011) 10350-10358.

[34] C. Wilke, P. Chang, Correlation of diffusion coefficients in dilute solutions, *AIChE Journal*, 1 (1955) 264-270.

[35] F.R. Brushett, Microfluidic platforms for the investigation of fuel cell catalysts and electrodes, University of Illinois at Urbana-Champaign, 2011.

- [36] C. Xu, A. Faghri, Mass transport analysis of a passive vapor-feed direct methanol fuel cell, *Journal of Power Sources*, 195 (2010) 7011-7024.
- [37] A. Verma, S. Basu, Experimental evaluation and mathematical modeling of a direct alkaline fuel cell, *Journal of power sources*, 168 (2007) 200-210.
- [38] R. Gilliam, J. Graydon, D. Kirk, S. Thorpe, A review of specific conductivities of potassium hydroxide solutions for various concentrations and temperatures, *International Journal of Hydrogen Energy*, 32 (2007) 359-364.
- [39] C. Xu, A. Faghri, Water transport characteristics in a passive liquid-feed DMFC, *International Journal of Heat and Mass Transfer*, 53 (2010) 1951-1966.
- [40] F.R. Brushett, Microfluidic platforms for the investigation of fuel cell catalysts and electrodes, University of Illinois at Urbana-Champaign 2010.

Figures:

Fig. 1 Schematic diagram of two different fuel feeding modes in MFCs: (a) Liquid-feed; (b) Vapor-feed.

Fig. 2 Computational domain of the present VF-MFC model (1-fuel evaporation surface, 2-vapor chamber, 3-gas diffusion anode, 4-anode groove, 5-electrolyte channel, 6-cathode groove, 7-gas diffusion cathode; The lower inset is a SEM image of the surface morphology of the anode GDL used in our previous experiment [6])

Fig. 3 Model validation with experimental data under various test conditions: (a) Different fuel concentrations; (b) Different electrolyte concentrations; (c) Different electrolyte flow rates

Fig. 4 Comparison between the VF-MFC and the LF-MFC: (a) Schematic diagram of the LF-MFC model; (b) Cell performance; (c) Fuel utilization.

Fig. 5 Fuel distribution inside the microfluidic channel of the: (a) VF-MFC (the left inset shows the distribution of local flow rates at a surface 0.01mm away from the anode CL); (b) LF-MFC.

Fig. 6 Effect of electrolyte flow rate on the VF-MFC: (a) Polarization curves; (b) Fuel concentration at anode and cathode CL at OCV; (c) Short-circuit current density and hydroxyl concentration at anode CL; (d) Fuel utilization.

Fig. 7 Effect of fuel evaporation area on the VF-MFC: (a) Distribution of vapor concentration inside the vapor chamber; (b) Polarization curves; (c) Fuel utilization at 0.3 V and fuel concentration at the anode CL at OCV.

Fig. 8 Effect of anode open ratio on the VF-MFC: (a) Distribution of dissolved fuel inside the electrolyte flow; (b) Polarization curves (absolute current and power output); (c) Fuel utilization and fuel concentration at the channel outlet; (d) Fuel concentration at the cathode CL.