A Counter-flow Microfluidic Fuel Cell Achieving Concentrated Fuel Operation

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Hao Zhang[a], Hong Xu[a], *, Li Zhang[a], Dennis Y.C. Leung[b], Huizhi Wang[c], Jin Xuan[a, c],*

[a]State-key Laboratory of Chemical Engineering, School of Mechanical and Power Engineering, East China University of Science and Technology, Shanghai, 200237, China
[b]Department of Mechanical Engineering, The University of Hong Kong, Hong Kong, China
[c]School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, United Kingdom

Abstract

Microfluidic fuel cell (MFC) is a considered as a promising energy source for powering portable electronic devices due to low cost and easy control. However, the energy density of MFC is much lower than conventional batteries like lithium battery. Due to the fuel crossover, the optimized operation concentration remains 1-2 M. In this paper, a counter-flow MFC is presented to achieve concentrated fuel. Density mismatch between fuel and electrolyte is the key cause for fuel crossover. Experimental and modeling study confirms that through adjusting different channel design according to fuel concentration, fuel crossover can be prevented.

Keywords: microfluidic fuel cell, concentrated fuel, high energy density

1. Introduction

Microfluidic fuel cell (MFC) holds the bright prospect as the next generation power source for portable devices. Since flow streams keeps in laminar pattern, physical barrier like membrane is eliminated, which largely reduces the cost of fuel cell. Excellent performance is achieved by MFC [1, 2]. Although MFC undergoes a rapid development since its first invention, there are still some bottlenecks should be broke through, one of which is low energy density problem [kjeang review]. The optimized fuel concentration for MFC is around 1 M [3, 4]. Take formic acid as fuel for instance, the corresponding energy density is 80 Wh L^{-1}, which is only about 20% of lithium battery [5, 6].

In this paper, an experimental and modelling study on counter-flow MFC is presented to improving the

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* Corresponding author. Tel: +86 21 64252847; fax: +86 21 64253810
Email address: jxuan@ecust.edu.cn; j.xuan@hw.ac.uk (J. Xuan).

operation concentration of fuel. It is found parasitic current caused by density mismatch is accelerated with fuel concentration growing, which restricts the improvement of fuel concentration. Therefore, flow velocity operation should be carried out to restrain fuel crossover.

2. Experimental section

In this study, a T-shaped counter-flow MFC was made of poly methylmethacrylate (PMMA). A CO_2 laser cutter (VLS 3.5, Universal) was used to fabricate the microchannel. As shown in Fig. 1, three sheets of PMMA were machined to form the microchannel. Platinum black loaded carbon paper (3 mg cm^{-2}) is used as anode, and a gas diffusion electrode composed of platinum black loaded carbon paper (3 mg cm^{-2}) is used as cathode. The final active area is 2×5 mm in width and length. Formic acid of 0.5-10 M supported by 0.5-2 M sulphuric acid was used as fuel and 0.5-2M sulphuric acid was used as catholyte. A syringe pump (LSP02-1B, Longer) was used to drive the flow streams and the flow rate was controlled in the range from 1-20 μL min^{-1}. An electrochemical station (CHI 660E, CH instrument) was used to measure the electrochemical performance of this MFC.
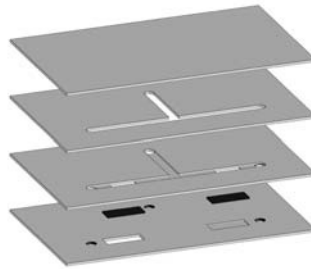
Fig. 1. Assemble schematic of counter-flow MFC

3. Numerical model

A computational model of counter-flow MFC is carried out to analyze current-voltage behavior, identify performance limiting factor and optimize cell performance.

In anode, fuel electro oxidation occurs:

$$2HCOOH \rightarrow 2CO_2 + 4H^+ + 4e^- \text{ (-0.22V vs SHE)}$$ (1)

At cathode, the oxygen reduction reaction takes place:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \text{ (1.229 vs SHE)}$$ (2)

The continuity equation, conservation equations of momentum and species are used to solve the hydrodynamics and species distribution:

$$\nabla \cdot (\rho u) = 0$$ (3)

$$\nabla \cdot (\rho u u) = -\nabla \cdot p + \nabla \cdot \tau + \rho g$$ (4)

$$\nabla \cdot \left(\rho \omega_i u \right) = -\nabla \cdot j + S_i \tag{5}$$

$$S_i = M_i \frac{\gamma_i \nabla \cdot i}{n_i F} \tag{6}$$

The density of formic acid solution is fitted using the experimental data in [7] :

$$\rho = 1011 + 208 \cdot \omega_f \tag{7}$$

The diffusion of formic acid is given by:

$$j_i = -\left(\rho D_i \nabla \omega_i + \rho \omega_i D_i \frac{\nabla M_n}{M_n} \right) \tag{8}$$

$$M_n = \left(\sum_i \frac{w_i}{M_i} \right)^{-1} \tag{9}$$

Since parasitic reactions occur at anode and cathode due to the reactant crossover, the parasitic effects should be taken into consideration. Because the anode is isolated from oxygen, and the concentration of dissolved oxygen is much smaller than fuel, it is reasonable to neglect the effect of crossover of oxygen [8]. The electrochemical kinetics at anode and cathode are given:

$$\text{Anode: } i_a = i_{a,0} \left(\frac{c_f}{c_{f,ref}} \right)^{\chi} \left(\exp\left(\frac{\alpha_a n_t F \eta}{RT} \right) - \exp\left(\frac{-\alpha_c n_t F \eta}{RT} \right) \right) \tag{10}$$

$$\text{Cathode: } i_{cm} = i_{c,0} \left(\frac{c_o}{c_{o,ref}} \right)^{\chi} \left(\exp\left(\frac{\alpha_a n_t F \eta}{RT} \right) - \exp\left(\frac{-\alpha_c n_t F \eta}{RT} \right) \right) \tag{11}$$

$$i_{cp} = i_{a,0} \left(\frac{c_f}{c_{f,ref}} \right)^{\chi} \left(\exp\left(\frac{\alpha_a n_t F \eta}{RT} \right) - \exp\left(\frac{-\alpha_c n_t F \eta}{RT} \right) \right) \tag{12}$$

$$i_c = i_{cm} + i_{cp} \tag{13}$$

$$\eta = \varphi_s - \varphi_l - E \tag{14}$$

The relationship between potential and current is:

$$-\sigma\Delta\varphi = S_k \tag{15}$$

$$S_k = \nabla \cdot i \tag{16}$$

The inlet flow velocity and outlet pressure was set to solve the hydrodynamics equations and no-slip condition was set at walls. In flow concentration was used to solve the concentration distribution. The key input parameters are listed in Table 1. COMSOL multiphysics 4.3b was applied to resolve the differential equations.

Table 1. Key input parameter of this model

Parameter	Intendment	Unit	Value	Refs
$c_{f,ref}$	Anode reference concentration	mol L^{-1}	1000	-
$c_{o,ref}$	Cathode reference concentration	mol L^{-1}	1.25	-
c_0	Saturated oxygen concentration	mol L^{-1}	0.25	[9]
i_a	Anode exchange current density	A m^{-2}	0.004	Fitted
i_c	Cathode exchange current density	A m^{-2}	0.06	Fitted
T	Absolute temperature	K	298	-
χ	Reaction order	-	1	[8]
α_a	Anode transfer coefficients	-	0.5	[8]
α_c	Cathode transfer coefficients	-	0.5	[8]
n_t	Eletron number at rate-limiting step	-	1	[9]
D_f	Diffusivity	m^2 s^{-1}	1.6×10^{-8}	Fitted

4. Results and discussion

4.1 Model validation

As shown in Fig. 2, the simulation results are in good agreement with experimental data, which indicates the validation of this model. The operation condition of experiment and simulation work is: 1 M formic acid supported by 0.5M sulfuric acid as fuel and 0.5M sulfuric acid as catholyte; flow rate as 10μL min^{-1}.
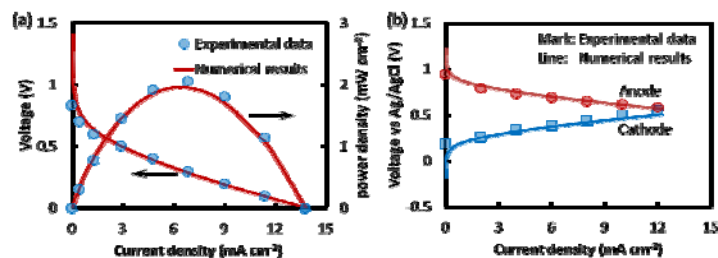

Fig. 2. (a) Current-voltage curve and current-power curve of counter-flow MFC; (b) current-voltage curves of single electrodes of counter-flow MFC.

4.2 Concentrated fuel operation

Fig. 3a shows the curve of power density of counter-flow MFC at 0.3V against fuel concentration. 2M of fuel is found to be the optimal concentration at 1 μL min-1. More concentrated fuel will lead to decrease in performance. The numerical results indicate that both main and parasitic current are intensified with concentration. However, parasitic current grows more rapidly than main current which generate an optimal fuel concentration corresponding to peak power density value. When fuel concentration exceeds the optimal concentration, further improvement in fuel concentration will cause performance recession. It is easily understandable that fuel crossover cause by diffusion is accelerated with fuel concentration. However, it is not diffusion crossover but gravity induced crossover which is found the main reason owed to result in such rapid intensification in parasitic current. The performance of counter-flow MFC without considering gravity is plotted against fuel concentration as shown in Fig. 3a. The result shows that intensification in diffusion crossover cannot prevent performance enhancement with fuel concentration.
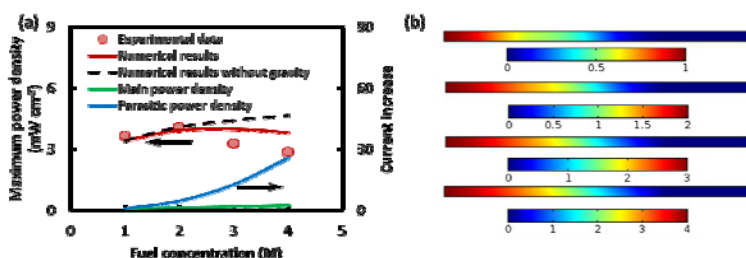

Fig. 3. (a) Curve of maximum power density and current increase of main and parasitic current against fuel concentration; (b) concentration distribution of fuel at different fed concentration. The current increase is calculated by dividing the each current value by the one at 1 M of formic acid.

As shown in Fig. 3b, with fuel concentration growing, the intensifying density difference between anolyte and catholyte reorients the interface of two streams. As a result, fuel stream crossover to cathode driving by gravity, which is the primary cause for restricting performance improvement with fuel concentration. In order to compress the gravity crossover and obtain high-concentrated fuel operation, higher flow velocity is needed. Cell performance against flow rate using 4M formic acid is shown in Fig. 4. It confirms that increase in flow rate is benefit for achieving high concentration operation.
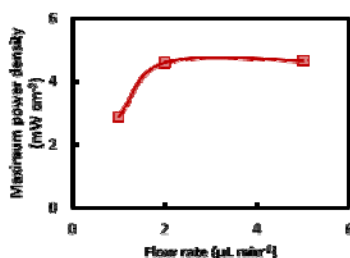

Fig. 4. Maximum power density against flow rate of counter-flow MFC using 4 M formic acid supported by 2 M sulfuric acid as fuel.

5. Conclusion

In this paper a T-shaped counter-flow MFC is proposed to increase the fuel operation concentration. It is found that the cell performance decreases with fuel concentration rising because of the fuel crossover. Unlike the other co-laminar MFC, the main reason for fuel crossover in counter-flow MFC is not induced by the diffusion but the gravity. Since the density mismatch between fuel and buffer electrolyte grows with fuel concentration increasing, the interface of anolyte and catholyte will reorient, which causes fuel crossover to opposite electrode. Increasing in flow velocity can restrain the reorientation, thus inhibit fuel crossover. Fuel concentration of 4 M was fed in this MFC and no performance reduction was induced at 2 µL min^{-1}. Further work should be carried out for more concentrated fuel operation.

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Acknowledgements

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Biography

Hao Zhang is a PhD student from East China University of Science and Technology. His research interests focus on microfluidic technology for energy conversion and sustainable energy.