

Short communication

Analyses of fuel utilization in microfluidic fuel cell

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Abstract

A microfluidic fuel cell is a miniature power source, which potentially could be used in micro electronic equipments, laptop computers, mobile phones and video cameras. In recent reports, the idea of a microfluidic fuel cell without using a polymer electrolyte membrane is proposed, whereby the laminar nature of the flow in the micro-channels is used to keep the anode and cathode streams separated such that adverse electrochemical reactions do not take place at the two electrode polarities. Since such cells are restricted by their size, improvement in fuel utilization would increase the cell efficiency by several degrees. In the present study, an improvement in fuel utilization is proposed by altering the design of the microfluidic fuel cell. In particular, a sulfuric acid stream is introduced between the fuel (HCOOH) and oxidizer (O_2 in H_2SO_4) streams to improve fuel utilization. Further improvement in fuel utilization is possible by changing the aspect ratio of the cell from 0.1 to 1. The fuel utilization of a cell with an aspect ratio of 0.1 is 14.1%, which increases to 16% when a sulfuric acid stream is introduced to prevent mixing of the fuel and oxidizer streams. The fuel utilization increases to 19% with the change in aspect ratio from 0.1 to 10, which further increases to 32% with the introduction of a sulfuric acid stream.

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1. Introduction

Investigations are being conducted world-wide in the field of miniaturization of fuel cell power sources. These are intended for use in portable devices such as laptop computers, mobile phones, video cameras and micro electronic equipments, which require a sustained supply of power without interruption for recharging or maintenance [1]. The emerging microfluidic fuel cell is a portable power source that offers the promise of providing power for longer hours without recharging. Normally in a fuel cell, fuel (H_2) and oxidizer (O_2) streams remain separated by a proton exchange membrane (PEM) which allows only protons (H^+) produced on the anode side to transfer to cathode side to take part in the oxygen reduction reaction. The PEM is a non-conductor of electrons and thus prevents short-circuiting of the cell. Many miniature models of the direct methanol fuel cell have been proposed in which the fuel and oxidizer streams remain separated

by the PEM [2,3]. Use of a PEM poses a size restriction on the fuel cell as difficulties in terms of drying out of the membrane, and thermal and water management are encountered. Further, fuel cross-over through the PEM is a major concern for direct methanol fuel cell.

Recently introduced membrane-less microfluidic fuel cells take advantage of the laminar nature of micro-channel flow to maintain separation of the fuel (HCOOH in H_2SO_4) and oxidizer (O_2 in H_2SO_4) streams [4–6]. A schematic of a microfluidic fuel cell is shown in Fig. 1. It should be noted that the separation of fuel and oxidant is required to prevent the oxidation and reduction reactions taking place at the adverse electrodes. Fuel and oxidizer are introduced at the inlet of the micro-channel and the electrodes are placed at the opposite walls to complete the microfluidic fuel cell structure. Acid electrolyte present in the fuel and oxidizer streams facilitates the transverse movement of protons by diffusion from the anode to the cathode. Thus, the length of the fuel cell is limited to mixing of the two streams such that the adverse electrochemical reaction is prevented.

Ferrigno et al. [5] performed experiments in a microfluidic fuel cell with a vanadium redox system and reported a fuel utilization of 0.1% for a $0.2\text{ mm} \times 2\text{ mm}$ cell and 10% for a

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Nomenclature

C_A	concentration of fuel (mol L^{-1})
C_{A0}	initial concentration of fuel (mol L^{-1})
D	diffusion coefficient of fuel ($\text{m}^2 \text{s}^{-1}$)
t	time (s)
V	velocity of fuel or oxidant in the cell (m s^{-1})
r_A	rate of reaction of A ($\text{mol L}^{-1} \text{s}^{-1}$)
x	x -coordinate axis
y	y -coordinate axis
z	z -coordinate axis

0.05 mm \times 2 mm cell. A membrane-less microfluidic fuel cell using formic acid as fuel and oxygen as oxidizer was demonstrated by Choban et al. [4,6]. They used a ‘Y’ shaped channel and demonstrated experimentally that two streams flowing parallel in a laminar regime remain separated, eliminating the need for a PEM. They reported fuel utilization of 0.1%. A detailed fabrication method for a membrane-less micro-channel fuel cell has been formulated by Cohen et al. [7]. They worked on a formic acid system and showed that the low power density was improved by incorporating an array of channels (stack) within a limited space. Bazylak et al. [8] performed CFD simulation of a ‘T’ shaped channel of different cross-sectional area and demonstrated that a square geometry with a 100 $\mu\text{m} \times 100 \mu\text{m}$ cross-section (aspect ratio 1) provided a fuel utilization of 3%. A rectangular geometry of 55 $\mu\text{m} \times 550 \mu\text{m}$ cross-section (aspect ratio 0.1) gave a fuel utilization of 8% at a 0.1 m s^{-1} velocity of the fuel and oxidizer streams. The fuel utilization increased to 23% at a 0.02 m s^{-1} velocity, and to 52% for a tapered channel. On the other hand, tapering increases the area of the electrodes by many fold and thus the cost of the cell would increase. They

stated that the degree to which the reactants are mixed at the interface is an indicator of the scope for further improvement in fuel utilization.

In this study, an analysis of membrane-less microfluidic fuel cells is presented in which an improvement in fuel utilization is achieved without much of an increase in cell size. The results show that a cell with a different aspect ratio may be used for such an improvement. Also, a new cell design with the introduction of a sulfuric acid stream between the fuel and oxidizer streams is proposed to minimize the mixing of fuel and oxidant streams and thus increase cell performance.

2. Theory and calculation

2.1. Hydrodynamic and mass transport model

Normally, a parabolic velocity profile is obtained for a steady, isothermal, incompressible flow in a micro-channel by solving Navier–Stokes and continuity equations while neglecting the body forces and heating due to viscous dissipation at a low velocity. In the microfluidic fuel cell, as the flow of the fuel and oxidizer streams are in the laminar region and they flow side-by-side through the micro-channel, the relative velocity of the two streams in contact with each other at the interface is assumed zero. The concentration of fuel in oxidizer stream near the interface due to diffusion is a function of the distance from the interface and the elapsed time of the two streams in contact with each other.

2.2. Diffusion at interface

The governing equation for the concentration of fuel, C_A , diffusing to cathode side is given by the following diffusion

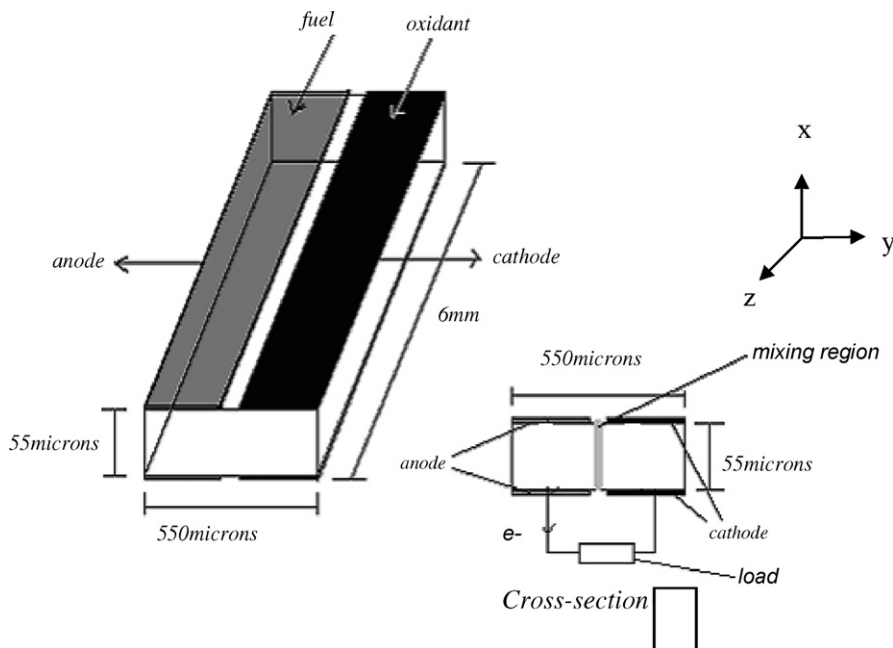


Fig. 1. Geometry of channel explored for improving fuel utilization with aspect ratio of 0.1. Anode reaction is $\text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$ and cathode reaction is $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$.

equation (Fig. 1):

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial y^2} \quad (1)$$

where the initial condition is $t=0, C_A=0$ and the boundary conditions are (1) $y=0, C_A=C_{A0}$; (2) $y \rightarrow \infty, C_A=0$. Initially, the fuel concentration in the cathode side is zero. The initial concentration of fuel, C_{A0} , is assumed for a 6-mm long channel [8]. At the fuel–oxidant interface, the fuel concentration is C_{A0} and at a well distant location is zero, D is the diffusion coefficient of fuel (formic acid) in aqueous sulfuric acid solution. The same governing equation is valid for the oxidant, which is diffusing to anode side and the corresponding oxygen concentration and diffusion coefficient of oxygen in sulfuric acid should be used.

2.3. Diffusion at wall

The equation for the concentration profile of fuel or oxidant with cell length (z -direction) and width (y -direction) for electrochemical reaction at electrodes situated on the walls of the microfluidic fuel cell is given by:

$$V \frac{\partial C_A}{\partial z} = D \frac{\partial^2 C_A}{\partial y^2} + (-r_A) \quad (2)$$

where V is the velocity of fuel and r_A is the rate of reaction of fuel. The same governing equation is valid for the oxidant, which is diffusing to the cathode and reacting. Thus, the corresponding oxidant velocity and rate of reaction should be used. Diffusion in the axial direction is neglected. The electrochemical reactions at the electrodes are assumed to be instantaneous as the fuel and oxidant concentrations are low. The velocity profile near the wall is approximated as linear and thus in Eq. (2), $V=ay$, where ‘ a ’ is a constant. This is justified since the concentration boundary layer is much smaller than the momentum boundary layer at the wall [4]. The initial condition is $z=0, C_A=C_{A0}$ and the boundary conditions are given by (1) $y=0, C_A=0$; (2) $y \rightarrow \infty, C_A=C_{A0}$. The boundary condition at $y \rightarrow \infty$ is used from the work of Bazylak et al. [8] as the depletion region at the electrodes is very small. The binary mixture is considered to be dilute and a diffusion coefficient of $D=5 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ is assumed for the fuel (formic acid), which is a typical value of the diffusivity of relatively small molecules in an aqueous sulfuric acid solution.

Bazylak et al. [8] showed that the depletion region at the electrodes and the mixing region at the interface have very small dimensions compared with the cell dimensions. Thus the governing equations relating to the concentration gradient near the depleted electrode region and the fuel–oxidant interface region are taken to be independent of each other. Electrokinetic phenomena are neglected as the concentration of ions is high. Eqs. (1) and (2) with boundary conditions are solved using a numerical technique (Matlab PDF solver) and the fuel utilization is calculated. The fuel utilization is defined as the ratio of the amount of fuel consumed at the electrode and con-

verted to current to the total amount of fuel delivered to the cell.

3. Results and discussion

3.1. Fuel utilization

Fig. 2(a) and (b) shows the concentration profile of fuel (formic acid) and oxidant (O_2 in H_2SO_4) at the electrode surface and the fuel–oxidant interface in the micro-channel. In a 6-mm long channel of dimension $55 \mu\text{m} \times 550 \mu\text{m}$ cross-section, the fuel or oxidant depletion layer thickness at the electrodes is $10 \mu\text{m}$ (Fig. 1). The depletion layer thickness of oxidant at fuel side, and vice versa at the oxidation-fuel interface, reaches $20 \mu\text{m}$ for the same microfluidic fuel cell (Fig. 2b). This signifies that fuel and oxidant cross-over through the interface do not meet the fuel and oxidant depletion layer thickness close to the electrodes and hence no adverse electrochemical reaction takes place. At an inlet velocity of 0.1 m s^{-1} , the fuel utilized at the wall is $2.2 \times 10^{-12} \text{ mol s}^{-1}$, while the fuel concentration at the interface decreases by $3.79 \times 10^{-13} \text{ mol s}^{-1}$. The initial number of moles entering is $1.57 \times 10^{-11} \text{ mol s}^{-1}$, which gives a fuel utilization of 14.1%.

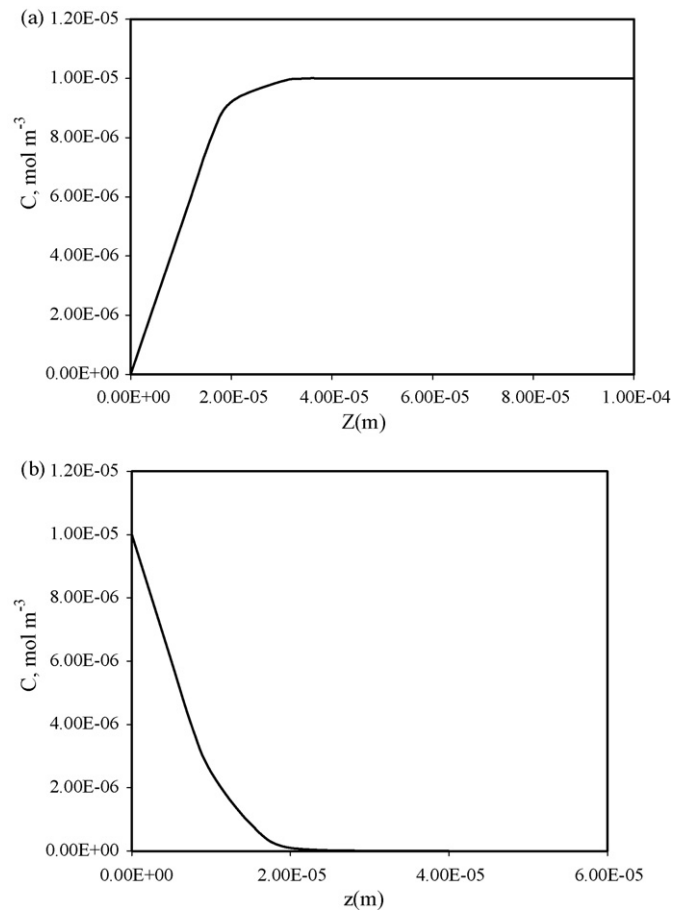


Fig. 2. (a) Concentration profile of fuel at electrode surface showing depletion region at end of 6-mm long channel of a microfluidic fuel cell and (b) concentration profile of oxidant at fuel–oxidant interface and at end of 6-mm long channel of a microfluidic fuel cell.

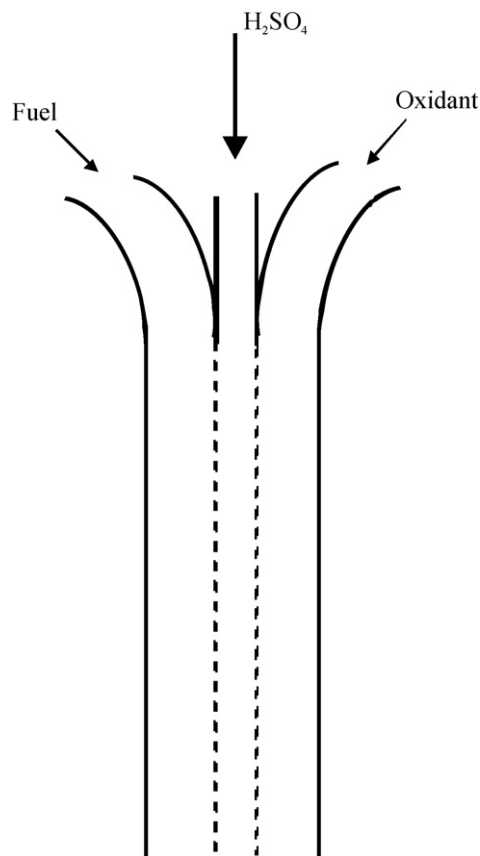


Fig. 3. Schematic showing presence of sulfuric acid stream between anode and cathode streams in microfluidic fuel cell.

3.2. Sulfuric acid stream

The fuel utilization slightly increases if a sulfuric acid stream is introduced between the anolyte and catholyte streams such

that no mixing between fuel and oxidant occurs. This is shown in Fig. 3. A passage of 20 μm width between the anode and the cathode stream is kept for the sulfuric acid stream, where no catalyst is present. With this design alteration, the concentration profiles would remain same since the boundary conditions mentioned earlier are valid. Thus, the moles of fuel utilized at the anode and the moles of fuel that are decreased at the interface would remain same. However, the fuel concentration introduced initially in the cell is reduced to $1.45 \times 10^{-11} \text{ mol s}^{-1}$ and hence fuel utilization increases to 16% from 14.1%.

3.3. Aspect ratio

The cell design (Fig. 4) is modified such that the aspect ratio is changed from 0.1 to 10, which leads to an increase in electrode area and fuel utilization to 19%. In this case, the distance between the electrodes (55 μm) is kept such that the depletion region of 10 μm thickness at the electrodes is achieved in a 6-mm long channel. Although the aspect ratio is changed, the boundary conditions at the interface remain the same as those discussed above. The width of the mixing region at the fuel–oxidant interface would remain as 20 μm for a 6-mm long channel (Fig. 4). The fuel used at the electrode is $3.1 \times 10^{-12} \text{ mol s}^{-1}$ and the fuel concentration decreases by $3.8 \times 10^{-13} \text{ mol s}^{-1}$ at the interface. Fuel is entering initially at $1.57 \times 10^{-11} \text{ mol s}^{-1}$, which gives a 19% fuel utilization. The fuel utilization is further improved if 20 μm of a sulfuric acid stream is introduced between the anode and the cathode streams and hence there is no loss of electrode area or fuel due to adverse electrochemical reaction. The fuel utilized and the decrease in fuel concentration at the interface remains unchanged as mentioned earlier. The fuel initially entering is $9.99 \times 10^{-12} \text{ mol s}^{-1}$ and thus the fuel utilization increases to 32%. The fuel utilization is increased

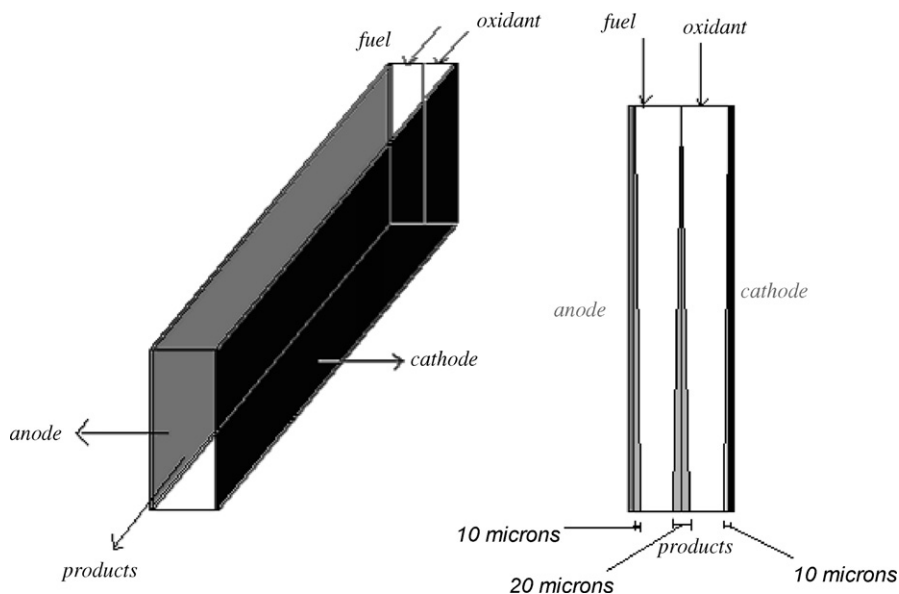


Fig. 4. Modified design of microfluidic fuel cell with aspect ratio of 10.

by considerable amount with change of aspect ratio from 0.1 to 10 and by introducing a sulfuric acid stream between the anode and cathode streams.

4. Conclusions

An improvement in fuel utilization of microfluidic fuel cells may be achieved by introducing a separate sulfuric acid stream between the anode and cathode streams and by changing the aspect ratio of the cell. The fuel utilization for an aspect ratio of 0.1 using formic acid as fuel is 14.1%, which increases to 16% when a sulfuric acid stream is introduced. With a modified cell design having an aspect ratio of 10, the fuel utilization increases to 19%, and then to 32%, when a sulfuric acid stream is introduced.

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