INTERNATIONAL JOURNAL of RENEWABLE ENERGY RESEARCH
Razieh Hassanshahi et al., Vol.3, No.4, 2013

Improved Control of Concentration Boundary Layer in Microfluidic Fuel Cells

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Received: 22.10.2013 Accepted: 14.11.2013

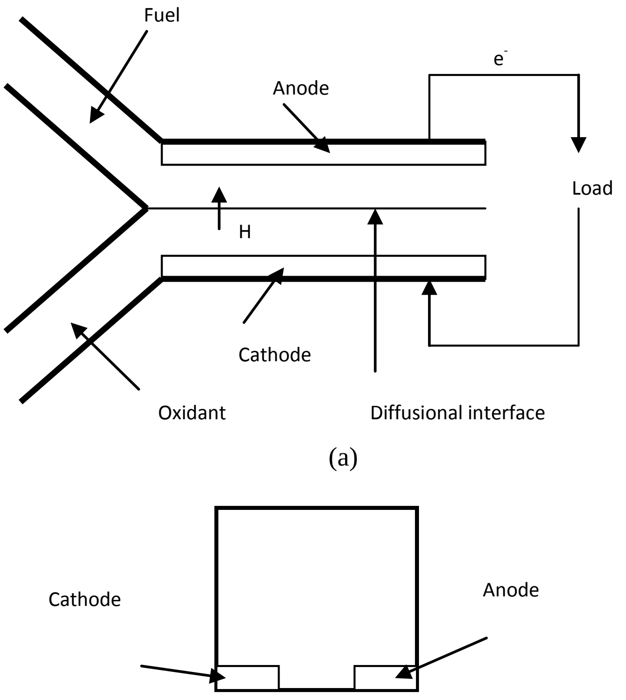
Abstract- In the current work, the enhanced structure for microfluidic fuel cell is proposed to improve the concentration boundary layer and raise the cell performance in consequence. Using COMSOL Multiphysics software and previously validated numerical model, the performance of the proposed design is investigated. Simulation results reveal that by splitting the electrodes which exist on the bottom wall of the microchannel and distributing them with distance on the bottom and top walls, the thickness of concentration boundary layer is controlled. In the proposed structure the electroactive area remains unchanged. By putting the split electrode on two walls of the microchannel there is no need to lengthen the microchannel. Lengthening the microchannel is undesirable because it can cause fuel crossover as the mixing region grows by lengthening the channel. As a result, this structure is better than the one in the past representing the split electrode on the one wall. In this sturcture, the maximum current density increases up to 60%.

Keywords microfluidic fuel cell, COMSOL Multiphysics, concentration boundary layer, laminar flow, microchannel, electrode

1. Introduction

There is a high demand for microscale power sources for small, portable applications. These power sources must be light in weight, have high power densities and be able to operate without being recharged for a long time. Miniature fuel cells can be a good alternative to batteries for small scale applications [1–4] due to their inherently high power and energy density. However, conventional fuel cell is difficult to be miniaturized because of its complicated system structures [5,6]. Machining graphite bipolar plates and the water management are difficult and the membrane can dried out. In addition, the supporting strength of the membrane and substrate decreases as a result of decrease in their size.

A recent, novel fuel cell architecture, called the microfluidic fuel cell, has shown great promise in addressing many of the problems above [6-9]. By utilizing the occurrence of laminar flow at low Reynolds number, streams of fuel and oxidant flow in parallel within a microchannel without needing a membrane to prevent them from mixing (fig. 1). Diffusion in a direction transverse to the flow creates a thin region around the liquid-liquid interface in the middle of the channel where the solution contains both fuel and oxidant. This region is called mixing region which limits the extension of the electrodes toward the middle of the channel (which is desirable since it increases the active surface area) due to the crossover issue. As the fuel and oxidant streams travel down the channel mixing region grows. A thin mixing region indicates better fuel/oxidant separation and this provides each side (anode and cathode) with more available reacting species. The fast rate of consumption of the reacting species at the electrodes results in the development of a concentration boundary layer (CBL). The CBL or depletion layer formed at the vicinity of the electrodes acts as a resistance for the reactants to reach the active surfaces. This layer gradually increases which slows down the reaction rate. In membraneless micro fuel cells, the depletion width is one of the major factors that determines the cell performance. Overcoming the mass-transfer limitations resulting from the presence of a depletion boundary layer on the reactive surface is key to improving the conversion efficiency. In this paper we will propose a new design for microfluidic fuel cell which enhances polarization curve and current density by controlling CBL. To explore the impact of the new design, the previously proposed numerical model in COMSOL Multiphysics is used [10].



(a)

(b)

Fig. 1. Configuration of the microfluidic fuel cell (a) top view (b) cross section of main channel.

To confirm the accuracy of COMSOL model used in this study the results obtained from the model simulation were compared with the results reported by Choban et al. [11] Due to some discrepancies between the two results, some model parameters such as diffusion coefficient and the cathode exchange current density were adjusted Since, the true value of exchange current density is not known and depends on some factors such as, surface roughness of the electrodes [12] and also the value used for diffusion coefficient was used by Chen et al. [13]. The results obtained from numerical simulation shown in fig. 2 confirm that the COMSOL model used in this study is a good tool to evaluate the effects of the new structure.

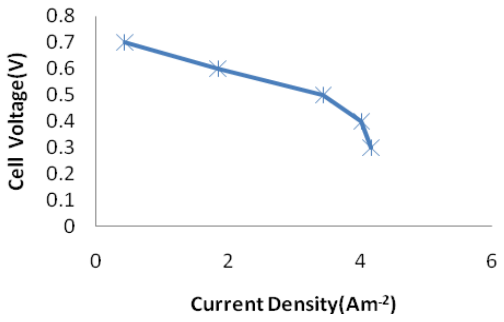


Fig. 2. the results obtained from numerical simulation

2. Theoretical Model and Formulation

The generation of electricity in the microfluidic fuel cells follows the electrochemical reactions at the anode and cathode. At the anode, formic acid decomposes and creates electrons and protons:

$$HCOOH \rightarrow CO^2 + 2H^+ + 2e^- \quad (1)$$

At the cathode, the oxygen reacts with the electrons coming from the anode and protons travelling across the channel to form water.

$$O^2+4H^++4e^-\rightarrow 2H_2O \quad (2)$$

Since the Reynolds number for microfluidic flows is normally low, the flow is laminar and incompressible. Therefore, Navier stokes and continuum equations are used to calculate the velocity field.

$$\nabla.v = 0 \quad (3)$$

$$\rho(v.\nabla v) = -\nabla p + \mu\nabla^2 v$$

Where, ρ and μ are the density and viscosity. v and p represent the velocity and pressure, respectively. Density and viscosity are both assumed to be equal for the two streams and constant over the whole domain.

In "Incompressible Navier-Stokes" module of COMSOL Multiphysics, the flow was assumed to continue into the electrode subdomains. The no-slip boundary condition was applied to all of the channel walls. A constant velocity was applied to the inlets, and the outlet was assumed to discharge to the atmospheric pressure.

Once the velocity field was calculated, it is possible to use the determined velocity to model the mass transport phenomena. In this model, the system is assumed to be isothermal, and pressure differences are not large enough to influence diffusion coefficients. Therefore, the concentration equation of species is defined by Fick's law

$$\nabla.(-D\nabla c + cv) = \frac{e_i}{nF} i \quad (4)$$

Where F reflects the Faraday constant, e and n are the mole number and the number of electrons transferred in the reaction, respectively. i reflects the rate of the electrochemical reaction in Eqs. (1) and (2) expressed by the volumetric rate of current generation which is calculated through Butler–Volmer equation.

In "Convection and Diffusion" module ,at the inlets, a uniform concentration is applied. At the outlet, the convective flux dominates mass transport and the concentration gradient normal to the outlet is set to zero. Insulation boundary conditions were applied to all of the channel walls. Within the electrode subdomains (where the species are consumed by electrochemical reactions), a source term is applied. Since the electrochemical reaction occurs at the anode and cathode only, i is equal to zero elsewhere in the system.

Transport of protons from the anode to the cathode is by electric migration only. To determine the electric field within the electrolyte and the solid-phase metallic electrodes, the following equations are used

$$\sigma\nabla.\nabla\phi_e = 0 \tag{5}$$

$$\sigma\nabla.\nabla\phi_s = 0$$

where ϕ_e and ϕ_s are the local potentials in the electrolyte and the solid-phase metallic electrodes, respectively.

In the “Conductive Media DC” module of COMSOL Multiphysics for electrolyte Electric insulation boundary conditions were applied to all of the channel surfaces. Within the electrodes, a current source is applied and the local current density is calculated by the Butler–Volmer reaction kinetics equation. In the “Conductive Media DC” module for solid-phase metallic electrodes since the metallic electrodes and current collectors are highly conductive, a large value for conductivity ($10^7 \mathrm{Sm}^{-1}$) was used. To have an uniform solid phase voltage, ϕ_s, over the entire subdomain a potential boundary condition for the outer electrode walls was applied. The electric insulation boundary conditions were applied to other boundaries.

In microfluidic fuel cell mass transfer limits the rate of the electrochemical reactions and the reaction rates are assumed to be linearly proportional to reactant concentration. Therefore, the modified Butler–Volmer equation is used to calculate the local current density across the electrode surface [12]:

$$i = ai_0 \frac{c}{c_{REF}} \left[e^{\left(\left(\frac{\alpha nF}{RT}\right)\eta\right)} - e^{\left(-\left(\frac{(1-\alpha)nF}{RT}\right)\eta\right)} \right] \tag{6}$$

where η represents the activation overpotential.

The reactant species are consumed at the rate of S [12]:

$$S = \frac{e_i}{nF} i \tag{7}$$

At each electrode, the activation overpotential required to overcome irreversibilities is calculated by Eq. (8) :

$$\eta = \phi_s - \phi_e - E_{REVERSIBLE} \tag{8}$$

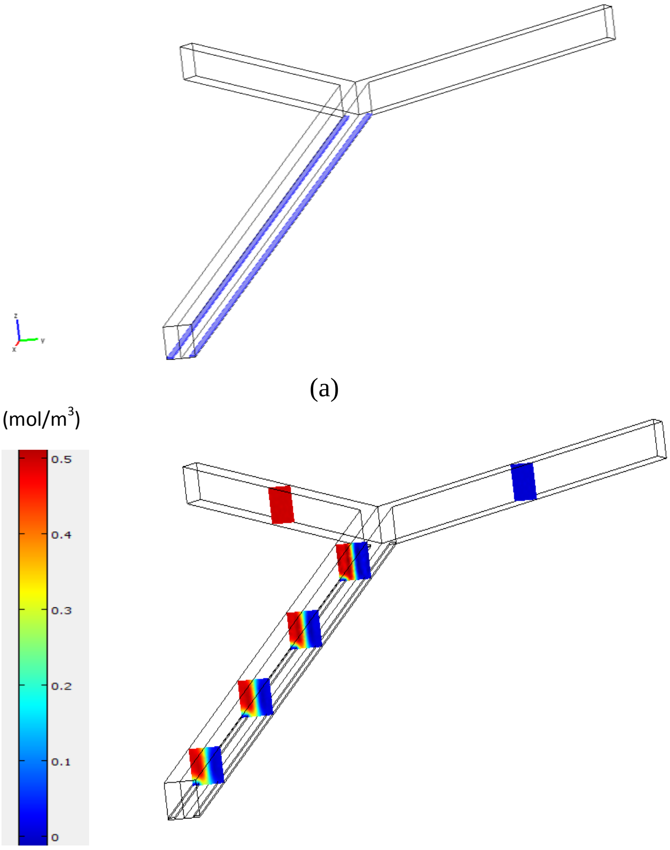
Where ϕ_s and ϕ_e is calculated by Eq. (5) and the reversible potential, $E_{REVERSIBLE}$, is taken as a constant value which is based on the reaction Gibbs free energy change at standard conditions.

3. Proposed Design

The performance of microfluidic systems that relies on surface interactions (e.g. fuel cells), is limited by either reaction kinetics or the rate of mass transfer to the reactive surfaces.

The focus of this paper is to present and analyze a new structure to enhance mass transport to a reactive surface and overall performance in consequence. Fig. 3 shows a schematic of a microfluidic fuel cell with electrodes on bottom wall.

The formation of depletion boundary layers on the electrodes takes place as a result of electrochemical reaction on the surface of the electrodes and mass transfer limitation. This prevents the reactants from reaching electrode surfaces.


(a)

(b)

Fig. 3. (a) a schematic of a microfluidic fuel cell with electrodes on bottom wall and (b) the density distribution of reactant particles(oxidant) in the channel

For optimal performance, i.e. high conversion rates at the electrode, it is important to maximize the rate by which the concentration boundary layer at the electrodes gets replenished. The thickness of the diffusion layer will vary above the surface of the electrode depending on the dimensions of the electrode and its position within the flow field.

The thickness of the diffusion layer for a planar electrode is calculated by Eq. (9): [14]

$$\delta \approx 3\left(\frac{D}{v}\right)^{\frac{1}{3}} \sqrt{\frac{vy}{U}} \tag{9}$$

where δ is the thickness of the diffusion boundary layer (cm), v the kinematic viscosity of the solution (cm^2/s), D the diffusion coefficient (cm^2/s), y the distance measured downstream from the leading edge of the planar electrode (cm), and U is the fluid velocity (cm/s).

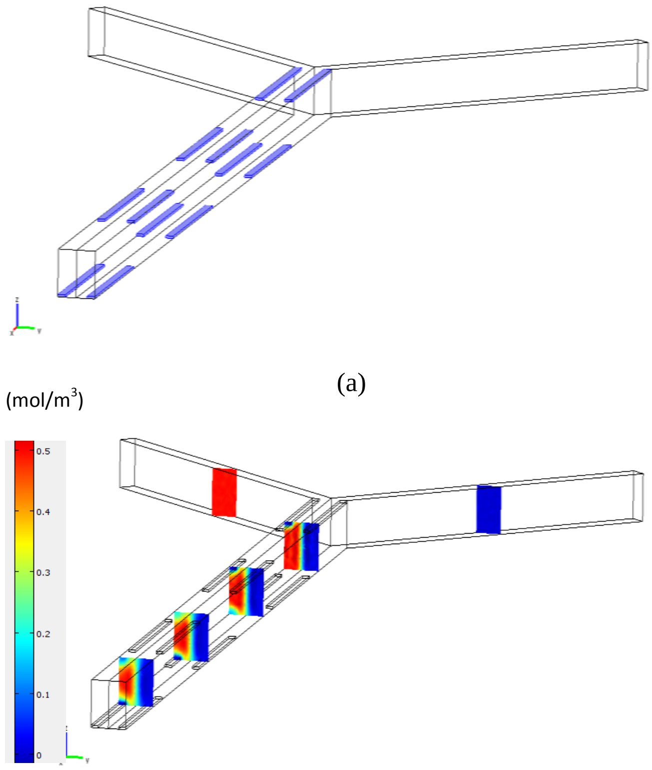
Thus, splitting a single electrode into two (or more) smaller electrodes and separating them, in other words, decreasing the distance measured from the upstream edge of the electrode provide a control on concentration boundary layer thickness [15].

Increasing the distance between multiple electrodes prevents a continuous increase in the diffusion layer that leads to a decrease in current density.

In the proposed design, we divided a single electrode on bottom wall to smaller electrodes and instead of placing them on only one wall of the channel [15], we put them on two walls of the channel (the bottom and the top).

Fig. 4 depicts the schematic of the proposed fuel cell and the density distribution of reactant particles in the channel.

The area of the electrodes in the proposed design is the same as the one in the simple design and separating the electrode prevents the increase in the thickness of concentration boundary layer.



(a)

(b)

Fig. 4. (a) The schematic of the proposed fuel cell and (b) the density distribution of reactant particles (oxidant) in the channel

To avoid fuel crossover (i.e. the reactants reaching the wrong electrode) due to the increase in the thickness of the diffusion layer in the longer channel (note that to have distance between electrodes and the same electroactive area, the channel must be longer),we put the separated electrodes on two walls of channel so that lengthening the channel to have separation between electrodes while having the same electrode area is not required.

Due to the fact that the concentration boundary layer is thinner at the beginning of the electrodes, reducing the length of them leads to higher power densities. The thinner the boundary layer, the higher the concentration gradient which generates higher current density.

To show the effect of this modification on the performance of the cell, figure 5 represents the polarization curve for simple microfluidic fuel cell and the proposed design. As seen in fig. 5, the new structure increases the cell current density by about 60%.

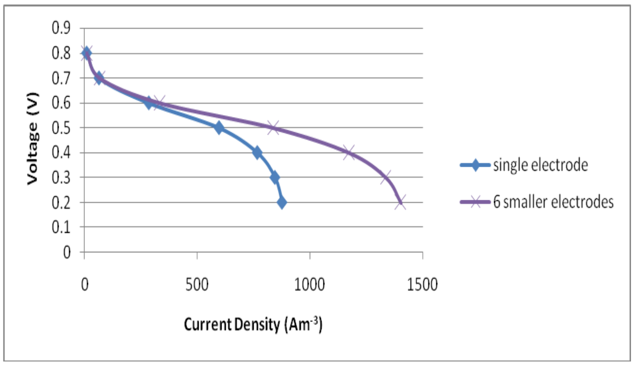


Fig. 5. The polarization curve of the proposed design.

4. Conclusion

Presented in this paper is an improved structure for microfluidc fuel cell to modify the performance of the cell through controlling the concentration boundary layer. The impact of the proposed design on performance of the cell was investigated by using a COMSOL numerical model. In the proposed design, the electrodes on the bottom wall of the microchannel are split to smaller electrodes and are replaced on both the top and the bottom walls. Applying distance between smaller electrodes prevents the concentration boundary layer from growing. Thus, the mass transport happens more easily and the performance of the cell is improved. To have the same electrode area while the electrodes are split and placed with distance, we put them on two walls of the channel, thus, there is no need to lengthen the micro channel while in the past work the spilt electrode was placed on only one wall. Lengthening the micro channel increases the possibility of fuel crossover due to the increase in the thickness of the mixing region. The proposed design could increase the maximum current density to about 60%.

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