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Computational modeling of alkaline air-breathing microfluidic fuel cells with an array of cylinder anodes

Ding-Ding Ye [a, b], Biao Zhang [a, b], Xun Zhu [a, b, *], Pang-Chieh Sui [c], Ned Djilali [c, d], Qiang Liao [a, b]

[a] Key Laboratory of Low-grade Energy Utilization Technologies and Systems, Chongqing University, Chongqing 400044, China
[b] Institute of Engineering Thermophysics, Chongqing University, Chongqing 400044, China
[c] Institute for Integrated Energy Systems, University of Victoria, P.O. Box 3055 STN CSC, Victoria, BC V8W 3P6, Canada
[d] Department of Mechanical Engineering, University of Victoria, P.O. Box 3055 STN CSC, Victoria, BC V8W 3P6, Canada

HIGHLIGHTS

- A 3D numerical model for alkaline air-breathing microfluidic fuel cells is developed.
- The anode current output is uneven and is correlated with internal ohmic resistance.
- A "fuel tunnel" exits in the anode array and can compensate axial current decline.
- Cathode potential reversal is caused by the boosted anode overpotential downstream.
- Anode current density distribution is relatively uniform along the flow direction.

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ABSTRACT

A three-dimensional computational model is developed for an alkaline air-breathing microfluidic fuel cell (AMFC) with an array of cylinder anodes. The model is validated against experimental data from an in-house prototype AMFC. The distributions of fluid velocity, fuel concentration and current density of the fuel cell are analyzed in detail. The effect of reactant flow rate on the cell performance and electrode potentials is also studied. The model results suggest that fuel crossover is minimized by the fast electrolyte flow in the vicinity of the cathode. The current production of each anode is uneven and is well correlated with internal ohmic resistance. Fuel transfer limitation occurs at low flow rates ($<100\ \mu L\ min^{-1}$) but diminishes at high flow rates. The model results also indicate that cathode potential reversal takes place at combined low flow rate and high current density conditions, mainly due to the improved overpotential downstream where fuel starvation occurs. The anode reaction current distribution is found to be relatively uniform, which is a result of a compensating mechanism that improves the current production of the bottom anodes downstream.

1. Introduction

Membraneless microfluidic fuel cells (MMFCs) eliminate the polymer electrolyte membrane by implementing a co-laminar fluid flow at microscale space. These fuel cells show great advantages of high energy density, high power density and feasible on-chip integration [1–4]. In particular, air-breathing microfluidic fuel cells (AMFCs) further eliminate the dissolved oxygen transfer limitation by integrating a gas diffusion electrode. Thus, AMFCs have been regarded as promising power sources for next generation portable electronic devices [2–5].

Various AMFC architectures have been reported [6–12], and most of them can be classified as planar and three-dimensional types based on their anode configuration. Overall, the planar type is the basic and well-studied AMFCs because of their simple structure. For practical applications, however, the main limitation lies in issues of fuel transport [9,13–15]. On one hand, the fuel transport to the anode is inherently limited by the fuel concentration boundary layer, thus leading to low cell performance. On the

* Corresponding author. Key Laboratory of Low-grade Energy Utilization Technologies and Systems, Chongqing University, Chongqing 400044, China.
E-mail address: zhuxun@cqu.edu.cn (X. Zhu).

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other hand, the bulk of the fuel stream does not participate in the anode reaction, resulting in low fuel conversion efficiency. Although the flow-through planar type AMFC can convectively replenish fuel depletion, the extra anodic flow channel inevitably reduces overall volumetric cell performance. Furthermore, since the fuel stream only permeates in the through-plane direction [8,9,15], insufficient hydraulic retention time within the thin catalyst layer can reduce fuel utilization rate. More importantly, the planar type AMFCs do not scale up well since the enlarged flow channel may destabilize the co-laminar flow [4,16–18].

Different from the conventional AMFCs with planar anodes, Zhu and Zhang et al. proposed a three-dimensional AMFC with an array of cylinder anodes [11]. Twelve anodes were connected in parallel and volumetrically stacked to provide spatially distributed circumferential catalytic surface area. The local fuel transport was convectively enhanced by the crossflow around the cylinder. Relatively high cell performance and high fuel utilization rate were achieved in the experiments. Moreover, the CO_2 bubbles produced by formic acid electro-oxidation were constrained in the array to minimize the perturbation to the cathode. More importantly, this cell architecture can be scaled up easily by extending the cylinder array either horizontally or vertically [19], while maintaining the identical interspace to preserve the co-laminar flow.

Nevertheless, the performance of such fuel cells was still limited by the sluggish reaction kinetics in the acidic electrolyte environment, and by the detrimental effects of trapped bubbles (e.g. anode coverage and improved internal ohmic resistance), especially at high current density conditions [11]. Furthermore, the dynamic behavior of CO_2 bubbles also creates fluctuation to current output. Recently, advantages of alkaline electrolyte have been demonstrated, since it can not only promote the reaction kinetics but also enable the use of non-noble catalysts [6,20–24]. More importantly, alkaline media inherently eliminates the two-phase flow effect, thereby resulting in stable cell performance. It is expected that operation in an alkaline environment can produce higher and stable cell performance, and it is more applicable in practical usage. However, the characteristics of fuel transport and current production in such alkaline fuel cells have not been well understood. More importantly, the interaction between fluid flow, mass transport and electrochemical reaction has not been elucidated for further development.

In this study, a three-dimensional computational model is developed for an alkaline AMFC with an array of cylinder anodes. The mass transport is resolved in a computational fluid dynamics (CFD) framework in conjunction with electrochemical reaction kinetics. The present model is validated against the experimental data from an in-house alkaline AMFC prototype. The distributions of fluid velocity, fuel concentration, anode current and ionic potential are analyzed in detail.

2. Numerical model

2.1. Computational domain

Fig. 1 schematically illustrates the computation domain. This fuel cell comprises 12 cylinder anodes and an air-breathing cathode. The anodes are arranged in a hexagonal pattern and are electrically connected in parallel. The possible shunt current is neglected, since it only occurs at high cell voltages and is much lower than the current output (not shown). Between the anodes and cathode, six electrical-isolated spacers are used to stabilize the interdiffusion region [11,19]. Given an inert and insulated material, the six spacers are replaced by through-holes. Detailed geometric parameters are listed in Table 1. Moreover, in order to determine anode current density and electrolyte potential, the main flow

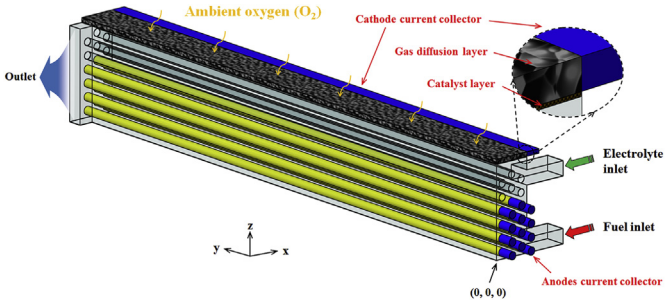

Fig. 1. Schematic illustration of the computational domain for alkaline AMFCs with an array of cylinder anodes.

channel is subdivided into ten sections along y direction (with identical length of 4 mm, not shown). In the computational domain, the present multiphysics model resolves the coupled mass transport of fluid, reactants and charged species in conjunction with electrochemical reactions. The whole system is assumed to be isothermal and at steady state.

2.2. Fluid flow

Both the fuel and the electrolyte streams are assumed to be laminar and incompressible, and are governed by continuity and the Nervier–Stokes equations:

$$\nabla \cdot \vec{u} = 0 \tag{1}$$

$$\rho\left(\vec{u} \cdot \nabla \vec{u}\right) = -\nabla p + \mu \nabla^2 \vec{u} \tag{2}$$

where u is the velocity vector, ρ the fluid density, p the pressure, and μ the dynamic viscosity. Body forces are neglected due to the microfluidic nature. The fluid density and viscosity are assumed to be constant. Detailed model parameters are listed in Table 2. The cathode catalyst layer is set as a subdomain, in which the fluid flow is continuous, whereas the fluid flow inside the gas diffusion layer is neglected due to the hydrophobic nature. Identical velocities are prescribed at the two inlets, while the outlet is set to ambient pressure. All other walls are non-slip boundaries.

In addition, the pumping power is determined by the following equation:

$$P = \Delta p_f Q_f + \Delta p_e Q_e \tag{3}$$

where Q_f and Q_e are the flow rate of the fuel and electrolyte, Δp_f and Δp_e are the pressure drop between the fuel/electrolyte inlet and outlet, respectively.

2.3. Mass transport

Dilute solution approximation is assumed for the fluid, i.e., the fuel conservation is written as:

$$\nabla \cdot \left(-D_f \nabla C_f\right) + \vec{u} \cdot \nabla C_f = S_f \tag{4}$$

$$S_f = -\frac{e i_a}{2F} \tag{5}$$

where D_f is the diffusion coefficient, C_f the local fuel concentration, F the Faraday constant (96,485 C mol^{-1}), e the mole number and i_a the anode current density determined by electrochemical reaction