Microfluidic fuel cell for off-the-grid applications

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Microfluidic Fuel Cell for off-the-grid Applications

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Abstract

The present doctoral thesis studies air-breathing microfluidic fuel cells with separated fuel and electrolyte streams as well as a membraneless fuel cell with selective electrodes. In order to gain more insight into the physio-chemical reactions, numerical simulation of the in-house developed air-breathing microfluidic fuel cell is formulated and solved using COMSOL Multiphysics. The results from the simulation show that fuel stream at the anode side and its interaction with the electrolyte stream has significant impact on the total fuel cell performance. As the first step for improving the hydrodynamic manipulation of the fuel stream, a flow-through porous anode is introduced. The effects of flow architecture on fuel utilization and the whole cell performance are investigated. Experimental results show that the flow-through porous anode improves the cell current in a long-term performance test as compared to the conventional design with flow-over planar anode. Because of the improved current generation, the rate of carbon dioxide generation in the cell increases. At high current densities, carbon dioxide produced in the channel emerges as bubbles that block and hinders reactant transport to the active sites of the anode.

Consequently, a new fuel cell design with fuel reservoir above the anode is introduced to address the issue of bubble formation. This design shows a higher and more stable long-term performance compared to the flow-through design. In addition, the air-breathing microfluidic fuel cell with fuel reservoir can use fuels with a high concentration. This new design provides a platform for stacking multiple cells.

Although the overall performance of air-breathing fuel cells has been improved significantly with the development route mentioned above, fluidic handlings of fuel and electrolyte streams in microfluidic fuel cells are still the main challenges from the perspective of practical applications. Consequently, a paradigm-changing membraneless fuel cell with a high open circuit potential of 0.60 V using hydrogen peroxide as both the fuel and the oxidant is introduced. In this design, hydrogen peroxide is both the electron acceptor and the electron donor over selective electrodes. Moreover, oxygen and water are the environmentally friendly products of the electrochemical reactions within the cell. Since a separating electrolyte medium is removed from the fuel cell, the whole system has the advantage of a very simple design of flow architecture which facilitates the potential integration of such device with actual applications. Mixing of anolyte and catholyte is not an issue and fuel recycling can be possible due to a single fuel stream. Design challenges remain only with the synthesis of high performance selective electrocatalysts. Further development of this membraneless hydrogen peroxide based fuel cell would open a new avenue for the field of micro power generation in lab-on-chip devices, point-of-care applications, and off-the-grid sensing.

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*Dedicated to my parents and all teachers who nurtured me with
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List of Publications

The following publications have been produced from this research work:

Refereed International Journal Papers:

[1] **S. A. Mousavi Shaegh**, Nam-Trung Nguyen, Siew Hwa Chan, “An Air-breathing Microfluidic Formic Acid Fuel Cell with a Porous Planar Anode: Experimental and Numerical Investigations”, *Journal of Micromechanics and Microengineering*, 2010, 20(10), 12 pp. (Selected paper (IOP Select) by editors of Institute of Physics for its novelty, significance and potential impact on future research.)

[2] **S. A. Mousavi Shaegh**, Nam-Trung Nguyen, Siew Hwa Chan, “A Review on Membraneless Laminar Flow-based Fuel Cells”, *International Journal of Hydrogen Energy*, 2011, 36(9), pp. 5675-5694

[3] **S. A. Mousavi Shaegh**, Nguyen, N-T, Chan, SH, Zhou, W, Air-breathing membraneless laminar flow-based fuel cell with flow-through anode. *International Journal of Hydrogen Energy* 2011, 37(4), pp. 3466-3476.

[4] **S. A. Mousavi Shaegh**, Nam-Trung Nguyen, Siew Hwa Chan, “Air-Breathing Microfluidic Fuel Cell with Fuel Reservoir”, *Journal of Power Sources* 2012, 29, pp. 312-317.

[5] **S. A. Mousavi Shaegh**, Nam-Trung Nguyen, Seyyed Mohsen Mousavi Ehteshami and Siew Hwa Chan, “Membraneless hydrogen peroxide fuel cell using Prussian Blue as cathode material”, *Energy & Environmental Science* 2012. 5(8): pp. 8225-8228

Refereed International Conference Papers:

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[2] **S. A. Mousavi Shaegh**, Nam-Trung Nguyen, Siew Hwa Chan, “Air-breathing membraneless laminar flow fuel cell with flow-through anode”, *Proceedings of the 9th Fuel Cell Science, Engineering and Technology Conference*, Aug 7-10, 2011, Washington DC, USA.

[3] **S. A. Mousavi Shaegh**, Yuli Huang, Nam-Trung Nguyen, Siew Hwa Chan, “Application of ion concentration polarization in a nanofluidic-based concentration”, *Proceedings of Second Conference on Advances in Microfluidics and Nanofluidics & Asia-Pacific International Symposium on Lab on Chip*, Jan 5-7 2011- Singapore.

Invited Book Chapter

[1] **S. A. Mousavi Shaegh**, Nam-Trung Nguyen, “Materials for Microfluidic Fuel cells” in “ Key Materials for Low Temperature Fuel Cells”, Eds. B. Ladewig, Y. Yan, S. P. Jiang, from book series of “The Wiley Series on New Materials for Sustainable energy and Development”, Ed. GQ Max Lu. **ISBN-10:** 3527330429.

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Table of Symbols

English Symbol	Description	Unit
c	Species concentration	mol m^{-3}
$C_{0, \text{HCOOH}}$	Reference concentration of formic acid	mol m^{-3}
C_{0, O_2}	Reference concentration of oxygen	mol m^{-3}
C_{0, O_2}	Reference concentration of oxygen	mol m^{-3}
D	Diffusion coefficient	$\text{m}^2 \text{s}^{-1}$
$D_{\text{O}_2(\text{water})}$	Diffusivity of oxygen in water	$\text{m}^2 \text{s}^{-1}$
$D_{\text{O}_2(\text{air})}$	Diffusivity of oxygen in air	$\text{m}^2 \text{s}^{-1}$
D_{HCOOH}	Diffusivity of formic acid as anolyte	$\text{m}^2 \text{s}^{-1}$
$D_{\text{O}_2(\text{water})}$	Diffusivity of oxygen in water	$\text{m}^2 \text{s}^{-1}$
$D_{\text{O}_2(\text{air})}$	Diffusivity of oxygen in air	$\text{m}^2 \text{s}^{-1}$
$E^0(T, P)$	Theoretical equilibrium open-circuit potential	V
f_1	Decay rate (Reaction rate constant)	s^{-1}
n_a	Number of transferred electrons at anode	
n_c	Number of transferred electrons at cathode	
F	Faraday's constant	Columb/mol
j_0	Exchange current density	A m^{-2}
j_{0a}	Exchange current density at anode	A m^{-2}
j_{0c}	Exchange current density at cathode	A m^{-2}
k	In-plane permeability of carbon-fiber-based paper	m^2
K	Electrical conductivity of electrodes	$(\Omega \text{ m})^{-1}$
Pe	Peclet number	
R	Universal gas constant	$\text{J mol}^{-1} \text{K}^{-1}$
R_{sf}	Scale factor	m
$R_{\text{electrolyte}}$	Ionic resistance of electrolyte	Ω

Re	Reynolds number	
T	Temperature	K
u	Velocity of fluid	m s^{-1}
U	Mean velocity of fluid	m s^{-1}
V	Potential	V
W	Height of the channel	m
x	Longitudinal coordinate	m
y	Lateral coordinate	m
z	Directional coordinate	m

Greek symbols

β	Inlet concentration, reaction order	mol m^{-3}
ΔG_1^+	Energy barrier between the reactant and activated states	
ε	Porosity of carbon paper used as GDE and anode	-
η	Overpotential	V
μ	Viscosity	$\text{kg m}^{-1} \text{s}^{-1}$
ρ	Density of anolyte and electrolyte stream	kg m^{-3}
τ	Tortuosity of carbon paper	

Superscript

0	Denotes standard or reference state
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Subscripts

a	Denotes the anode
c	Denotes the cathode
i	Denotes a species
x	Denotes the first derivative of a function with respect to x

xx	Denotes the second derivative of a function with respect to x
y	Denotes the first derivative of a function with respect to y
yy	Denotes the second derivative of a function with respect to y
$*$	Denotes a dimensionless variable

List of Abbreviations

GDE	Gas Diffusion Electrode
OCV or OCP	Open-circuit voltage (potential)
LFFC	Laminar Flow Fuel Cell
ORR	Oxygen reduction reaction
3D	Three Dimensional

Chapter 1 Introduction*

**This chapter was partly published in the following papers:*

- [1] Mousavi Shaegh, S.A., Nguyen, N.T., Chan, S.H., 2011. A review on membraneless laminar flow-based fuel cells. *International Journal of Hydrogen Energy* 36, 5675-5694.
- [2] Mousavi Shaegh, S.A., Nguyen, N.T., Chan, S.H., Zhou, W., Air-breathing membraneless laminar flow-based fuel cell with flow-through anode. *International Journal of Hydrogen Energy*, 2012. 37(4): p. 3466-3476.

1.1 Background and Motivation

Advancement in miniaturization technology leads to the emergence of a new class of power generating devices for low-power applications [1]. Small-scale energy conversion schemes are referred to as micro power generation [2]. Generally, micro power generation can be categorized as (i) chemical-based conversion including micro internal combustion engines and micro gas turbine engines [2]; (ii) electrochemical-based conversion such as batteries and fuel cells [3]; and (iii) solid-state direct energy conversion such as thermoelectric and photovoltaic microstructures [2].

The proliferation of portable microelectronic devices and off-the-grid sensors used in biological, environmental and security monitoring applications leads to a high demand for miniaturized and reliable electrical power sources. A miniaturized high-energy-density power source to maintain long-term operation is a critical requirement for these applications. Since electrochemical power generators do not have moving parts and can be fabricated by relatively simple fabrication processes [4], they are suitable power sources for the applications mentioned above.

Currently, the major power sources for portable electronics and off-the-grid applications are batteries [3]. Demands for longer operation time without frequent recharging has motivated the research community to enhance the energy density of batteries, or to deploy alternative power sources such as micro fuel cells [3]. A power consumer usually has two different demand modes: (i) low-power-demand mode where the device is in sleep or in monitor operation, and (ii) high-power-demand mode where the device requires high power for transmitting data or actuation [5]. To meet the energy requirements of both low-power-demand and

high-power-demand modes, a fuel cell can work under steady-state operating conditions to recharge a secondary battery for the burst-power occasions.

Fuel cell technology can potentially take advantage of fuels with energy densities of an order of magnitude higher than that of batteries [6]. Nevertheless, if the weight or volume of the ancillary components, reactant reservoirs and fluidic handling channels are considered, the advantage of high energy density remains only for few mobile systems [7]. Consequently, miniaturization is necessary to make a fuel cell compatible for the integration with small and portable power consumers. Bibliographic analysis of published academic papers shows a recent trend of rapid growth in miniaturization of fuel cells using micro fabrication technologies, Figure 1.1.

In order to exploit a miniaturized fuel cell or a micro fuel cell (MFC) as a long-lasting power source, key challenges and major issues have to be addressed. Micro fuel cells generally exploit proton exchange membrane running on methanol or hydrogen with close or open (air-breathing) cathode [8, 9]. One of the main issues of current fuel cells is associated with the proton exchange membrane. Keeping high proton conductivity of membranes such as Nafion for different operation modes is challenging. Water management adds further complexity to the fuel cell system. Fuel crossover through the membrane is another detrimental issue that degrades the overall cell performance. Swelling and shrinkage of the membrane during water uptake and dehydration deforms the membrane resulting in packaging failure. Consequently, miniaturization of a fuel cell system is more than just downsizing a large-scale fuel cell and its auxiliary components by using microfabrication techniques.

Ideal integrated MFC system should be highly independent from conditioning systems using passive and self-regulating fuel/oxidant delivery schemes. Different components of a MFC should be fabricated in a monolithic manner in connection with fuel and oxidant delivery systems. Typical miniaturization and integration research activities on MFCs are the development of monolithic structure with integrated electrodes and membrane on porous silicon with minimum membrane humidity conditioning and high proton conductivity [10], microreactors for hydrogen production from methanol [11], self-regulating hydrogen generator based on metal hydrides [6, 12], passive or self-circulation fuel/oxidant delivery with built-in CO₂ bubble removal system [13-15] and membraneless fuel cells [7, 16-18].

Membraneless fuel cells are generally fabricated in a single compartment. The membrane is removed entirely from the fuel cell structure. The removal of the membrane enhances the flexibility in cell miniaturization [18]. Membraneless fuel cells are generally classified into two main categories: (i) fuel cells with selective electrodes such as biofuel cells, micro direct methanol fuel cell with a selective air-breathing cathode for oxygen reduction [18-21], one compartment fuel cells running on hydrogen peroxide as both fuel and oxidant [16], and (ii) micro fluidic fuel cells in which mixing of fuel and oxidant is restricted to a confined liquid-liquid interface.

Miniature bio fuel cells use enzyme catalysts, and can run on oxygen and glucose. Because of their biocompatibility and very low power density on the order of 1 $\mu\text{W}/\text{cm}^2$, miniature bio fuel cells are potentially suitable for powering medical sensors and transmitters implanted in the body [7]. In addition to low power outputs, bio fuel cells require particular conditions of pH, temperature and

reactant concentration for the survival of the biocatalysts restricting the range of their application.

Micro direct methanol fuel cells with a selective air-breathing cathode for oxygen reduction has a power output of up to 2 μ W[18, 20], which is very low for most practical applications.

One-compartment fuel cells run on hydrogen peroxide as both fuel and oxidant with selective electrodes has recently gain attention as an environmentally friendly and carbon-free mean of power generation. [16, 22, 23]. Since only one reactant is utilized in the fuel cell, fluidic handling does not need further auxiliary components such as two separate reservoirs and complex fluidic channels which add enormous flexibility to the design and the fabrication of a fuel cell system. Hydrogen peroxide-based fuel cells can be selected as a strong platform for micro fuel cell technology with a performance not achieved before. Further developments for enhancing the reaction kinetics should be carried out for this fuel cell type.

The development of laminar flow-based fuel cell (LFFC), known as microfluidic fuel cell [24] or membraneless fuel cell [17], is an attempt to provide a simplified fuel cell design with a higher level of integration. Although the total number of research works on micro fuel cells has reached a plateau from 2009, Figure 1.1, but micro fluidic fuel cells have gain attention in recent years, Figure 1.2. Since its introduction in 2002, many investigations have been focused on further explorations of the coupled hydrodynamic and electrochemical reactions in microfluidic fuel cells, Figure 1.2.

Figure 1.1 Bibliographic analysis of publications using keyword of Micro Fuel Cell. Data were extracted from online version of SciVerse ScopusTM of Elsevier B.V. SciVerse ScopusTM is a bibliographic database containing abstracts and citations for academic journal articles.

Microfluidic fuel cells take advantage of the lamination of fuel and oxidant streams in an aqueous supporting electrolyte in a microchannel. Charge transport between the electrodes occurs inside the channel and through the co-laminar liquid-liquid interface. Since the membrane is removed from the cell structure, a LFFC resembles a microelectrochemical reactor. In addition to power generation, a modified design of LFFC can provide a simple but convenient and reliable platform for characterizing the performance and durability of electrodes and catalysts [25].

Current designs of microfluidic fuel cells are still far from deployment in real applications. Since a solid state membrane does not exist in microfluidic fuel cells, electrochemical reactions are highly twisted with hydrodynamic conditions of fuel

Figure 1.2 Bibliographic analysis of publications using keyword of Microfluidic Fuel Cell. Data was extracted from online version of SciVerse ScopusTM of Elsevier B.V. SciVerse ScopusTM is a bibliographic database containing abstracts and citations for academic journal articles.

and oxidant streams flowing in a cell. More investigations should be carried out to study the effect of cell hydrodynamic conditions on electrochemical reactions.

1.2 Objectives and Scope

The first objective of this project is to gain insights into key parameters and their effect on the overall performance of membraneless microfluidic fuel cells. The major research effort is focused on unfolding the highly interrelated hydrodynamic and electrochemical phenomena that exist in a microfluidic fuel cell. The second objective is the search for a new catalyst to improve the overall performance of membraneless hydrogen peroxide-based fuel cells.

To achieve the above objectives, the research work and the corresponding thesis are organized into the following chapters:

Chapter 2 includes the literature review on the state of the art and provides perspective on further development opportunities of microfluidic fuel cells.

Chapter 3 describes the fabrication and experimental methods for the characterization of air-breathing microfluidic fuel cells reported in this thesis.

Chapter 4 provides detailed insight into the physico-chemical phenomena in an air-breathing fuel cell using numerical simulation.

Chapter 5 explores the effect of flow architecture on the performance of microfluidic fuel cells with flow-over and flow-through porous anodes.

Chapter 6 proposes a new design for air-breathing microfluidic fuel cells with fuel reservoir to improve the overall performance and mass transport within the cell.

Chapter 7 investigates a proof-of-concept of exploiting a new catalyst for the cathode side of a membraneless fuel cells using hydrogen peroxide as both fuel and oxidant.

Chapter 8 summarizes and provides a perspective on potential future works.

The information and data provided in the thesis would open new avenues for further development of membraneless fuel cells for portable applications such as off-the-grid sensors and labs on a chip.

Chapter 2 Microfluidic Fuel Cells: Literature Review and Potential Opportunities*

**This chapter was partly published in:*

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Abstract:

This chapter reviews the flow architectures of microfluidic fuel cells. The review offers better understanding of the influence of hydrodynamic manipulation on the overall performance of these fuel cells. In addition, state of the art of published designs and further development opportunities are discussed.

2.1 Operation of a Microfluidic Fuel Cell

Microfluidic fuel cells or membraneless laminar flow-based fuel cells (LFFCs) follow the basic electrochemical principles of membrane-based fuel cells. The only difference is that the membrane as a charge transport media and as a separator of electrodes is replaced by a liquid-liquid interface in a microchannel. Microchannels are defined here as channels with a characteristic dimension less than 1 mm and greater than 1 μm [26]. The manipulation of fluid flow in microchannels is based on microfluidic technology.

The ratio of surface area to volume $\frac{R_{sf}^2}{R_{sf}^3} = R_{sf}^{-1}$ increases with miniaturization,

where R_{sf} is the scale factor. Thus, surface phenomena dominate over volume based phenomena in microscale. Microfluidic systems take advantage of the scale-dependence of interface properties to exploit a wide range of applications [27]. As the size of fluidic systems decreases, laminar regime at low Reynolds numbers governs the behavior of fluid flow in microchannels. As mentioned above, surface-based effects such as surface tension or viscous drag dominate over volume-based effects, offering new interesting microscale phenomena. For instance, a stable liquid-liquid interface can be achieved in a microchannel with co-laminar streams.

As shown in Figure 2.1(a), when two separate streams of fuel and oxidant are introduced into a microchannel, a parallel co-laminar flow with a stable liquid-liquid interface is established. This interface plays the role of a separator between fuel and oxidant streams. Current collectors and electrodes with appropriate catalyst layer on the surface are deposited on the channel walls where the electrochemical reactions take place. To obtain charge transport between the two

electrodes, both fuel and oxidant solutions could have a high ionic conductivity by adding supporting electrolyte. The supporting electrolyte contains hydroxide or hydronium ions such as diluted solutions of potassium hydroxide or sulfuric acid. Ohmic losses are mainly attributed to the ionic resistance $R_{electrolyte}$ of the electrolyte and the external resistance of electrodes and connections $R_{external}$ when current i is drawn from the cell:

$$\eta_r = i \cdot (R_{electrolyte} + R_{external}) \quad (2.1)$$

The Ohmic resistance of the supporting electrolyte depends on anode-to-cathode spacing as the charge-transport length d , cross-sectional area of the charge transport A , and the ionic conductivity σ :

$$R_{electrical} = \frac{d}{\sigma A} \quad (2.2)$$

Typical bulk through-plane conductivity of Nafion[®] as proton exchange membrane is around 0.1 S/cm at 100% relative humidity (RH) and room temperature [28] with a typical membrane thickness of 50 to 200 μm . In contrast, the conductivity of 0.5 M sulfuric acid as a common supporting electrolyte is in the order of 0.2 S/cm. Anode to cathode spacing in a membraneless LFFC is generally in the range of 0.5 mm to 1.5 mm resulting in a higher total Ohmic loss as compared to conventional PEM fuel cells. A simple “concept map” is plotted in Figure 2.2 to provide an overview on the interacting phenomena and their influence on the performance of a microfluidic fuel cell.

Figure 2.1 Flow-over designs; (a) Schematic sketch of a membraneless LFFC with side-by-side streaming in an Y-shape channel; (b) A-A cross-section of the channel, schematic sketch of configuration of both electrodes at bottom wall; (c) Cross section of the channel showing depletion boundary layers over anode and cathode and interdiffusion zone at the liquid-liquid interface with vertical electrodes and side walls; (d) Cross section of channel with top-bottom electrodes configuration; (e) Cross section of a channel with both electrodes on the bottom wall in a grooved channel; (f) Cross section of a channel with graphite rods as electrodes.

Figure 2.2 A general and simplified concept map to describe the effect of cross-related active mechanisms on the performance of a membraneless laminar flow-based fuel cell.

2.2 Membraneless LFFCs Designs and Flow Architectures

The interface between two streams with supporting electrolytes represents a virtual membrane by providing (i) an ion conductive media and (ii) effective and controlled mixing of reactants across the cell. Membraneless LFFCs can benefit from the following features of microfluidics:

- (i) The membrane is eliminated thus reducing the size of the cell and enhancing the flexibility in cell design and fabrication [17, 18].
- (ii) Since both streams flow through a single channel, design considerations for fuel and oxidant delivery systems are less complicated thus simplifying sealing and packaging. Furthermore, the composition of fuel and oxidant streams can be tailored individually to maximize reaction kinetics at anode and cathode [29].
- (iii) Membrane-related issues such as water management, membrane fouling and membrane damage partially disappear [17, 30].
- (iv) Membraneless LFFC as a power source is compatible with other microfluidic systems such as lab-on-chip devices.

Low fuel utilization per single pass and low power output are considered as the major drawbacks of membraneless LFFCs. Since both electrodes and streams are usually placed in a single channel, the flow architecture of the streams has significant effects on the performance of membraneless LFFC. In the past, many investigations were carried out to study the influence of flow architecture and electrode arrangements on the performance of a membraneless LFFC.

Depending on the type of implemented electrodes, membraneless LFFC are categorized as (i) flow-over type with planar electrodes, (ii) flow-through type with three-dimensional porous electrodes, and membraneless LFFC with air-breathing cathode. All designs exploit common fuels and oxidants and can be fabricated by conventional methods with the same level of precision. All designs can use either alkaline or acidic electrolytes.

2.3 Flow-over Electrodes

2.3.1 Electrode Location

As shown in Figure 2.1, two electrodes of a membraneless LFFC are usually implemented in a microchannel. The fuel and oxidant streams come into contact in two configurations: side-by-side streaming with vertical fuel-oxidant interface and vertically-layered streaming with horizontal fuel-oxidant interface. For both streaming configurations, the two electrodes can be positioned on top and bottom walls, Figure 2.1(b), side walls, Figure 2.1(c), or both electrodes on bottom wall, Figure 2.1(d). In addition, the electrodes can be positioned in a grooved channel, Figure 2.1(e), to control the effect of bubble formation on liquid-liquid interface. An array of electrodes can also be implemented in the channel as shown in Figure 2.1(f).

For the vertical interface of co-laminar streams, gravity-induced reorientation of the interface may occur, if fuel and oxidant streams have different densities. As both streams flow down the channel, the denser fluid is forced by gravity mismatch to gradually occupy the lower portion of the microchannel [31]. Due to this reorientation, the operation of a membraneless LFFC begins to fail since fuel oxidation and oxidant reduction are no longer restricted to the right electrodes. Thus, for a horizontal liquid-liquid interface, the mismatch of densities may speed up the broadening phenomenon of inter-diffusion zone if the denser fluid is on top.

Flow-over designs generally provide streaming of fuel and oxidant over planar electrodes. Only a fraction of fuel and oxidant streams adjacent to the catalyst layer participate in electrocatalytic reactions. Due to the lack of effective convective mass transport, a depletion boundary layer with low reactant

concentration grows over both electrodes. To enhance fuel utilization in flow-over designs, a flow-through electrode was implemented to provide a larger active area for electrochemical reactions Figure 2.1(f) [30].

2.3.2 Carrier Substrate

Microchannels are typically fabricated by rapid prototyping techniques, using standard photolithography, soft lithography or laser micro-machining. In some designs of membraneless LFFCs with side-by-side streaming, the channel structures are fabricated using poly dimethylsiloxane (PDMS) molding and sealed to a solid substrate with electrodes [32, 33]. For sealing the channel, glass or PDMS treated with oxygen plasma can be used. In addition, the channels are made hydrophilic by exposing them to oxygen plasma. PDMS is useful for making microfluidic devices due to its properties such as easy fabrication (rapid prototyping, sealing, easy interconnects), transparency in the UV-visible regions, chemical inertness, low polarity, low electrical conductivity, elasticity and low-cost fabrication [34].

Due to the relatively high diffusivity of hydrogen and oxygen in PDMS ($D_{H_2} = 1.4 \times 10^{-4} \text{ cm}^2/\text{s}$ and $D_{O_2} = 34 \times 10^{-5} \text{ cm}^2/\text{s}$ at 35°C) [35], gas reactants can be supplied through thin layers of PDMS to a pair of electrodes separated by a channel containing sulfuric acid or sodium hydroxide as electrolyte [36, 37]. Using this concept, the power densities of the cells running on dissolved hydrogen/oxygen [37] and hydrogen/air [36] were around 0.7 m/Wcm^2 as restricted by permeation rate of hydrogen through PDMS.

Figure 2.3 Carrier substrate with different layers of membraneless LFFCs: (a) Vertical electrodes with vertical liquid-liquid interface; (b) PMMA based membraneless LFFC with horizontal electrodes; (c) Silicon-based microchannel for membraneless LFFC with horizontal flow-over electrodes.

Choban et al. [29] used graphite as a substrate to serve three functions: current collector, catalyst support, and edificial element. As shown in Figure 2.3(a), the graphite plates are placed side-by-side with a spacer to form the flow channel. The catalyst is applied to the graphite plates before assembling. To seal the channel, 1-mm thick polycarbonate slabs with a thin film of PDMS were used as the gasket.

Polymethylmethacrylate (PMMA) is another polymeric material frequently used in micro fuel cells [8]. PMMA is one of the thermoplastic polymers that are linearly-linked and can be softened by applying heat above the glass transition temperature [38]. PMMA has a non-crystalline structure with 92% light transmittance in the visible spectrum. This material also has other excellent properties such as low frictional coefficient, high chemical resistance and good electrical insulation. All the above features and properties make PMMA a good substrate for microfluidic devices, especially for those involved in chemical applications [38].

A PMMA substrate can be micro-machined in many ways such as X-ray exposure and subsequent development, hot embossing and laser machining [38]. In case of laser machining, the cross section of the microchannel depends on the shape of laser beam, its moving speed, laser power and thermal diffusivity of substrate material. Since energy of a laser beam has a Gaussian distribution, thus a cross section of an engraved channel by laser beam also has a Gaussian shape [38].

Li et al. [39] used an infrared CO₂ laser to engrave channels in PMMA to fabricate a membraneless fuel cell. In their design, three PMMA sheets are used to form the channel, Figure 2.3(b). A slit is cut into a 1-mm thick middle sheet using the same laser. The channel is covered by two PMMA sheets using a dry adhesive layer. The bottom layer works as the electrode support and liquid sealing plate. A 100 nm gold layer was sputtered on the surface of the PMMA sheet to reduce the contact resistance. This gold layer acts as the current collector. The surface of the PMMA sheets was mechanically treated with fine sandpaper (1200 grit) to improve the surface roughness and the adhesion of the gold layer to the substrate. Outlet and inlet holes were machined in the top PMMA sheet. Pt-Ru and Pt catalyst inks were wet-sprayed on the gold layer to make anode and cathode with a loading of 4.5 mg/cm², respectively.

Rigid microchannels were also fabricated in silicon using photolithography [40, 41]. Since silicon is stable against thermal deformation, silicon channels and substrates can be used to investigate temperature dependent oxidation and fuel cell performance [40]. In this design, platinum is deposited on the adhesion layer using E-beam evaporation technique. Exploiting standard photolithography for silicon processing, the design benefits from the ease of fabrication where parameters can

be varied. Therefore, optimization of microchannel dimension can be carried out in a relatively short time period [40], Figure 2.3(c).

2.4 Fuel and Oxidant Delivery Schemes

Fuel and oxidant concentrations over anode and cathode decrease because of the on-going electrooxidation of fuel and electroreduction of oxidant within a cell. Thus, because of the lack of convective mass transport to replenish fresh reactants to the catalytic active area, a depletion boundary layer over the catalyst-covered electrodes is formed [42].

The current density is a function of reactant concentration. If effective replenishment of depletion layer does not happen, the reactant concentration over the active area of electrodes decreases and consequently the current density drops dramatically. In this way, only the first few millimeters of the electrode contribute the most to current collection [43]. In addition, the length of the channel must be restricted in order to control diffusive mixing and consequently parasitic losses [44].

To overcome the limitation of mass transport to active sites, Yoon et al. [42] introduce three methods to enhance the performance of a membraneless LFFC by controlling the depletion boundary layer, as shown in Figure 2.4. Mass transport to the planar active areas on the channel walls can be enhanced by (i) using “multiple inlets” to add fresh reactants to the microchannel and to replenish the depletion zones; (ii) removing the depleted zone through multiple outlets, and (iii) implementing herringbone ridges to supply the depleted layers with fresh reactant from the middle of the microchannel. Adding ridges to one wall increases 10 to 40% current density.

Approaches (i) and (ii) are most appropriate for enhancing the reactant conversion rate because they remove or replenish depletion zones providing a continuous high concentration of reactants above the active area. These approaches are suitable for enhancing the power density. Approach (iii) is suitable for enhancing fuel utilization in a single pass leading to higher reactant conversion efficiency. However, in terms of packaging and fabrication, approaches (i) and (ii) benefit more from a single-height design, but require more space for the multiple inlets/outlets. It is noteworthy that the pumping energy for approaches (i) and (ii) is larger than approach (iii).

The idea of passive control of the depletion layer to achieve a higher current density without consuming additional power led to investigations on the effect of multiple consecutive electrodes on the current density and fuel utilization [45, 46]. Lim et al. [45] proposed that each electrode can be made of an array of microelectrodes in length with a specific spacing between microelectrodes. Splitting the length of an electrode into two or more sections can avoid the continuous growth of the depletion layer. Thereby, a 25% increase in maximum power density compared to a single-electrode device with identical active area was achieved. Lee et al. [46] optimized the electrode length and gap between the consecutive electrodes using numerical simulation of a membraneless LFFC running on 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS) and oxidized ABTS. Incorporating the very small electrodes within the membraneless LFFC should maximize the current density while decreasing the amount of unspent fuel.

Figure 2.4 Three approaches for improving mass transport to control the depletion layer over electrodes: (a) Multiple inlets to add fresh reactants; (b) Multiple outlets to take out periodically the depleted zone; (c) Integrated herringbone ridges to supply reactants from the middle of channel to the depleted zone by transverse, spiraling flow, reproduced after [42].

2.4.1 Flow-Through Designs

In a flow-through design, the reactant streams pass through a three-dimensional porous electrode including the catalytic active area. In some designs, as depicted in Figure 2.5, the whole streams pass through a three-dimensional (3D) electrode. In other designs, the fuel and oxidant streams are divided into sub-streams, providing the so-called “multiple inlets” approach to refresh the depletion boundary layer, Figure 2.5(b). Because of the effective diffusive/convective mass transport through the 3D electrodes, the depletion boundary layer is replenished continuously resulting in a higher rate of fuel utilization and a greater power output. Flow-through design can provide an approximately constant concentration of reactant over active site for electrocatalysis.

Salloum et al. [47] proposed a membraneless LFFC with porous disk electrodes, Figure 2.5(a). The carrier substrate is fabricated in PMMA. Formic acid in sulfuric acid as fuel stream was introduced through an inlet from the centre of the disk and undergoes oxidation through a porous anode made of carbon paper covered with catalyst nanoparticles. The oxidant stream, potassium permanganate

in sulfuric acid, is introduced concentrically through a ring of inlets. Oxidant was reduced and then mixed with the oxidized fuel and a 2-mm gap between anode and cathode preventing a short circuit due to backflow of the oxidant.

The improvement of ion transport was improved due to convection increases the fuel utilization up to 58% and enables control of fuel and oxidant flow rate independently. Experimental results indicate that by increasing the fuel flow rates, fuel utilization decreases from 58% at 100 $\mu\text{l}/\text{min}$ to 4% at 5 ml/min . Increasing the concentration of sulfuric acid as supporting electrolyte, increases the maximum power density from $\sim 1.5 \text{ mW}/\text{cm}^2$ to $\sim 3 \text{ mW}/\text{cm}^2$ due to decreasing Ohmic losses. The concept of the so-called “multiple inlets” was developed by Sinton’s research group [48].

A flow-through design for adding fresh reactants was proposed without using a fluidic network. The whole cell was fabricated in PDMS. As shown in Figure 2.5(b), hydrophilic porous fiber-based carbon paper used for making gas diffusion layer in proton exchange membrane fuel cell (PEMFC) was cut into strips and placed in two compartments. High porosity of carbon paper, $\sim 87\%$ (HGP-H 90 from Toray) provides a large surface area for electrochemical reactions and enhances fuel utilization due to the improved diffusive/convective mass transport [48]. Running the cell on all-vanadium redox species, a peak power density of $131 \text{ mW}/\text{cm}^2$ with a net power of 16 Watts was obtained at a flow rate of 300 $\mu\text{l}/\text{min}$.

Figure 2.5 Flow-through designs: (a) Radial flow architecture for a membraneless LFFC, reproduced after [47]; (b) Three-dimensional flow-through porous electrodes with so-called "multiple inlets" concept.

2.4.2 Air-breathing Designs

Mass transfer and low diffusivity of oxygen dissolved in aqueous media ($2 \times 10^{-5} \text{ cm}^2/\text{s}$) limits the performance of membraneless LFFCs. In addition, low concentration of dissolved oxygen in aqueous media (2-4 mM) cannot sufficiently replenish the depletion boundary layer over the cathode. Exploiting a gas diffusion electrode (GDE) on a side wall of channel facilitates a cell to access a high concentration of oxygen in air (10 mM) with a diffusivity of $0.2 \text{ cm}^2/\text{s}$, which is four orders of magnitude higher than that in aqueous media.

Proof-of-concept of membraneless LFFC with an air-breathing cathode was proposed by Kenis' research group in 2005 [49]. As shown in Figure 2.6(a) and Figure 2.6(b), gas diffusion electrode (GDE), made of Toray carbon paper covered with catalyst ink containing platinum black nanoparticles, was implemented on the wall as an air-breathing cathode. The channel was made of PMMA which is glued to a graphite plate covered with palladium black nanoparticles as the flow-over anode.

Since the oxidant stream is eliminated in this design, a stream of electrolyte is needed to separate the fuel stream from direct exposure to the cathode avoiding fuel crossover losses and catalyst poisoning. A solution of 1 M formic acid was used as fuel while a solution of 0.5 M sulfuric acid available in both fuel and electrolyte streams facilitated proton conduction across the channel. A peak current density of 130 mA/cm^2 , and a power density of 26 mW/cm^2 were achieved using 300 ml/min at a fuel-to-electrolyte flow rate ratio of 1:1. Anode and cathode potentials obtained using a reference electrode revealed that oxygen concentration is not the source of limiting performance for an air-breathing membraneless LFFC [50].

To provide a quantitative comparison, the performance of membraneless LFFCs based on different electrode designs is listed in Table 2.1. Since the fuel type has significant effects on cell kinetics, only membraneless LFFCs running on formic acid or methanol are discussed. Table 2.2 also provides some design features and the maximum power density of three fuel cell types, including LFFC with flow-over anode, LFFC with flow-through anode and LFFC with air-breathing cathode.

Table 2.1 shows that the order of magnitude for the power density of membraneless LFFCs varies from 0.1 mW/cm^2 to 1 mW/cm^2 for the flow-over

Figure 2.6 Membraneless LFFCs with air-breathing cathodes: (a) Schematic illustration for the arrangement of fuel and electrolyte streams in the channel, reproduced after [49]; (b) Cross section and carrier substrate of the channel depicted in (a).

design, and from 1 to 10 mW/cm² for flow-through design. The low performance of flow-over designs is mainly attributed to low oxidant concentration at catholyte and the growth of depletion layer over electrodes. The improvement of performance for flow-through design is associated with the enhancement of catalytic reaction through porous and 3D electrodes due to the effective replenishment of reactant over active sites. The main reason for higher performance of membraneless LFFCs with air-breathing electrodes is the higher rate of oxygen transport to cathode from ambient air. Since oxygen is provided from air through GDE, the oxygen concentration over the active site of the cathode is almost constant, enhancing the current generation.

Table 2.1 Performance of LFFCs running on formic acid or methanol, reproduced after [24]

Design	Fuel/Oxidant	Electrolyte	Electrode structure	Maximum current density (mA/cm ²)	Maximum power density (mW/cm ²)	Design features
Choban et al. [29]	Methanol (1 M) Dissolved oxygen	Sulfuric acid or Potassium hydroxide (1 M)	Flow-over	40	12	Mixed media operation
Choban et al. [51]	Methanol (1 M) Dissolved O ₂	Sulfuric acid (0.5 M)	Flow-over	8	2.8	—
Cohen et al. [40]	Formic acid (0.5 M) Dissolved O ₂	Sulfuric acid (0.1 M)	Flow-over	1.5	0.18	Stackable microchannels
Choban et al. [52]	Formic acid (2.1 M) Dissolved oxygen	Sulfuric acid (0.5 M)	Flow-over	0.8	0.17	—
Li et al. [39]	Formic acid (0.5 M) Dissolved O ₂	Sulfuric acid (0.1 M)	Flow-over	1.5	0.58	Laser-machined
Morales-Acosta et al. [53]	Formic acid (0.1, 0.5 M) Dissolved oxygen	Sulfuric acid	Flow-over	11.5	3.3	Pd/MWCNTs as catalyst
Salloum et al. [47]	Formic acid (0.04 M) Potassium permanganate (0.01 M)	Sulfuric acid (0.5-1 M)	Flow-through	5	2.8	Sequential radial flow

Table 2.1 (cont.). Performance of LFFCs running by formic acid or methanol, reproduced after [24].

Design	Fuel/Oxidant	Electrolyte	Electrode/flow structure	Maximum current density (mA/cm ²)	Maximum power density (mW/cm ²)	Design features
Kjeang et al. [33]	Formic acid (1.2 M) Sodium hypochlorite (0.67 M)	Sodium hydroxide (2.8 M)	Flow-through	230	52	3D structure of electrodes
Jayashree et al. [49]	Formic acid (1 M) Air	Sulfuric acid (0.5 M)	Air-breathing	130	26	—
Jayashree et al. [50]	Methanol (1 M) Potassium hydroxide (1 M) Air	Sulfuric acid (0.5 M)	Air-breathing	120	17	—
Brushett et al. [54]	HCOOH (1 M) Air	Sulfuric acid (0.5 M) or potassium hydroxide (1 M)	Air-breathing	130	26	—
Hollinger et al. [55]	Methanol (1 M) O ₂	Sulfuric acid (1 M)	Air-breathing	655	70	Methanol @ 80 C with O ₂ feed to the cathode
Whipple et al. [56]	Methanol (0.1-15 M) Air	Sulfuric acid (0.5 M)	Air-breathing	62	4	Using Ru _x Se _y as methanol-tolerant catalyst for cathode

Table 2.2 Design features of three different electrode architectures with maximum power density running by formic acid or methanol.

Reference	Maximum power density (mW/cm ²)	Design features and comments
Flow-over electrode		
Choban et al.[29]	12 at flow rate of 3 ml/min per inlet flow	Side-by-side streaming, Y-shape, channel length of 29 mm, channel height of 1mm and channel width of 0.75 mm, Pt/Ru and Pt black nanoparticles in Nafion-based ink solution applied to graphite plate as anode and cathode, Fuel utilization <10%.
Flow-through electrode		
Kjeang et al. [33]	52 at 0.4 V and flow rate of 60 μ l/min per inlet	Side-by-side streaming, T-shape, channel length of 12mm, channel height of 0.3 mm, channel width of 3mm, electrodeposited Pd and Au on carbon paper strips to make flow-through anode and cathode, Fuel utilization of 85% at peak power density and 100% at lower voltages.
Air-breathing cathode		
Hollinger et al. [55]	70 at flow rate of 0.3 ml/min per inlet	Vertically layered streaming, T-shape geometry, channel length of 48 mm, channel width of 3.3 mm, Pt/Ru and Pt nanoparticles in Nafion-based ink solution brushed on carbon paper as electrodes, graphite plates as current collectors, implementation of a nanoporous separator at the fuel-electrolyte interface, running at 80 °C with O ₂ supply of 50 sccm, hot pressed thin film of Nafion over cathode to alleviate fuel crossover effects.

2.5 Performance Limiting Factors

To identify the performance limiting factors of membraneless LFFCs, experimental and theoretical approaches including using a reference electrode [50, 51] and numerical simulation of the coupled transport phenomena and electrochemical reactions have been reported [43, 46, 57-63]. The main objective of using a reference electrode is to measure the voltage losses due to different limiting parameters of an electrochemical system such as reaction kinetics, mass transfer and Ohmic resistance of individual electrodes [64]. The reference

electrodes can be used to identify and to provide solutions for the problems in a fuel cell [64].

Choban et al. [51] utilized external reference electrodes to identify the limiting factors of a membraneless LFFC. The current-voltage curve shows the mass transport limitation at high current densities, but this experiment does not identify whether this limitation takes place at the anode or the cathode. By using an external Ag/AgCl reference electrode, connected to the membraneless LFFC, the individual contribution of each electrode loss to the overall cell performance was determined. The results showed that the mass transport at the cathode is the limiting factor at high current densities for this specific design due to the low solubility of oxygen in water-based electrolyte [51].

Jayashree et al. [50] used an external Ag/AgCl reference electrode to identify the mass transfer limited electrode in a membraneless LFFC with an air-breathing cathode running on 1 M methanol. Supporting electrolytes of 0.5 M H₂SO₄ or 1 M KOH were used to investigate the effect of acidic or alkaline electrolyte on the whole cell performance. The shape of cathode polarization curve confirmed that the gas diffusion electrode allowed higher rate of oxygen transport to the cathode as compared to a membraneless LFFC running on dissolved oxygen.

2.5.1 Inter-diffusion mixing zone and fuel crossover

In addition to the low oxidant concentration over the catalytic areas and the slow mass transfer [65], diffusive mixing at the liquid-liquid interface can be considered as another major issue. Two consequences of diffusive mixing which degrades the overall cell performance and efficiency are: (i) reduction in the fuel/oxidant concentrations of fuel/oxidant streams with decreasing current density, and (ii) fuel crossover to cathode side leading to degradation of open-

circuit potential. Since platinum is usually used for oxygen reduction at the cathode side, fuel crossover and fuel oxidation over Pt can block the catalytic active sites. The adsorbed CO intermediates decrease the rate of electroreduction of oxygen at the cathode.

At low Reynolds number ($Re < 1$), two separate streams can be brought together allowing particles and ion to diffuse [66]. There are two mechanisms facilitating proton transport from anode to cathode: (i) diffusive transport due to the gradient in proton concentration between anode and cathode and (ii) electromigration due to the voltage gradient between the electrodes. By balancing the charge flux generated by a given voltage gradient and the highest attainable charge flux the voltage required to produce an equivalent charge flux is [67]:

$$V = \frac{RT}{zF} \quad (2.3)$$

where R and T are the universal gas constant and the temperature, respectively; z is the valence of the species and F is Faraday's constant.

At room temperature and $z = 1$, a voltage drop of 25.7 mV across the thickness of the ion conductor has the same effect as the maximum chemical driving force provided by the concentration gradient. Since membraneless LFFCs generally work at room temperature, the charge transport across the channel filled by electrolyte is dominated by electrical driving force rather than the chemical potential driving force.

Inter-diffusion width between two streams is highly dependent on the mean residence time of streams in the channel. The mean residence time is determined by the dimensions of the channel width, the channel height, the channel length and the input flow rate [68]. In co-laminar streams with different viscosities, the

channel width is mainly occupied by the more viscous fluid, which also moves with a slower mean velocity [68].

Diffusive broadening is the main cause of reactant crossover. The main effects of fuel crossover are the reduction of fuel concentration over the anode and the decrease of open-circuit potential due to mixed potential.

In a detailed study, Sprague et al. [69] calculated the parasitic crossover current at both anode and cathode of a membraneless LFFC with top/bottom arrangement of planar electrodes running on aqueous oxidant and fuel. The model utilizes the Poisson-Nernst-Planck (PNP) equations that provides a more general treatment of reactant crossover. Other models in the past assumed that the crossover reactant is fully utilized over the electrode producing crossover current [70]. The new model can capture the concentration change of crossover reactant along the opposite electrode. Results from this model show that decreasing the channel height (electrode-to-electrode spacing) increases fuel crossover and decreases open-circuit potential. Calculations were carried out for the narrowest channel with a height of 50 μm in two cases without and with the crossover current. At the given operating conditions of a membraneless LFFC, the open-circuit potential drops from 0.9 V without crossover to 0.1 V with crossover. The potential distribution across the channel was significantly affected by the reactant crossover. These observations suggest a reconsideration of common assumptions used in the modeling and simulation of reactant crossover in fuel cells.

2.6 Optimization of Channel Geometry

Since membraneless LFFCs generally exploit co-laminar flows in a single channel, flow structure has significant effects on the interaction between two streams. Bazylak et al. [71] established a 3D CFD model to simulate a

membraneless LFFC. In their numerical simulation, coupled electrochemical and mass transport phenomena were solved to simulate the depletion and mixing regions of formic acid and dissolved oxygen. Numerical results showed that both microchannel and electrode geometry play key roles for mass transport and inter-diffusion zone. Among different designs, a rectangle with both high aspect ratio (length/width) and tapered electrodes was proposed as an optimum design, Figures 2.7(a) and 2.7(b). Using the extended electrode designs, fuel utilization was improved by 50% while minimizing fuel-oxidant mixing in membraneless LFFC. The areas of cathodes and anodes and the gap between them must be set precisely to avoid the overlap between the diffusively mixed region and the electrodes. Numerical analysis revealed that by decreasing the inlet velocity from 0.1 to 0.02 m/s, the fuel utilization increases from 8% to 23% while there is only 3% increase in cross-stream mixing at the outlet.

In a numerical optimization of channel geometry, Ahmed et. al [72] explored the effect of a Ψ -shape geometry on fuel utilization and mixing width. Streams of 0.5 M formic acid in 0.1 M H_2SO_4 and 1.25 mM dissolved O_2 in 0.1 M sulfuric acid were separated by a stream of 0.1 M sulfuric acid solution working as proton-conducting fluid. Three streams are introduced into the cell from three separate inlets, Figures 2.7(c) and 2.7(d). Optimizing the channel dimensions and reaction surface areas, fuel utilization can be improved by up to 86%. Because of the restricted mixing of fuel and oxidant through the proton-conducting channel, this flow configuration is suitable for portable applications with random motions.

Figure 2.7 Electrode geometry optimization: (a) Tapered electrodes after [71]; (b) Cross section of channel presented in (a); (c) Introducing a blank electrolyte stream into the channel; (d) Cross section of channel illustrated in (c), reproduced after [72].

Sun et al. [73] introduced a blank electrolyte stream of 0.5 M H_2SO_4 into a Ψ -shaped microchannel to separate two streams of 2.1 M formic acid and 0.144 M potassium permanganate as shown schematically in Figures 2.7(c). Experimental results indicated that the optimized flow rate can enhance the open-circuit potential which is an indication for controlling the diffusion crossover of fuel. Using the concept of blank electrolyte stream, Salloum and Posner [74] proposed a counter-flow membraneless LFFC with 2 M sulfuric acid as separating electrolyte stream to control diffusive mixing of 50 mM vanadium redox species in 1 M sulfuric acid, Figures 2.8(a). A peak power density of 5 mW/cm^2 was observed at a fuel/oxidant flow rate of $300 \text{ } \mu\text{l/min}$ and electrolyte flow rate of $30 \text{ } \mu\text{l/min}$.

Another strategy to reduce the fuel crossover is implementing a thin nanoporous separator at the interface of the two streams [55, 75], in the expense of increasing design and packaging complexity and fabrication cost. Hollinger et al. [55] positioned a thin layer of polycarbonate with 0.05 μm pore size and density of 6×10^8 pores/ cm^2 at the fuel-electrolyte interface which reduces the liquid-liquid contact between two streams by 98.8%, Figure 2.8(b). The separator is not selective to methanol and may also reduce the proton transport across the channel. The diffusion coefficient of protons in an aqueous medium ($D_{\text{H}^+ (\text{water})} = 9.31 \times 10^{-9} \text{ m}^2/\text{s}$) is one order of magnitude higher than that of methanol ($D_{\text{MeOH} (\text{water})} = 1.58 \times 10^{-9} \text{ m}^2/\text{s}$). Moreover, proton diffusion is facilitated by the potential gradient between the electrodes while the only driving force for methanol transport is the concentration gradient across the channel. Hence, the separator has a greater effect on the mitigation of methanol crossover than the rapid proton transport phenomenon. This design improvement decreases the electrode-to-electrode distance. The rate of fuel diffusion to the electrolyte decreases significantly. The catalyst layer of the cathode was covered by a thin layer of Nafion using a hot press process. Since the diffusion coefficient of methanol in Nafion is one order of magnitude lower than that in water ($D_{\text{MeOH} (\text{Nafion})} = 3.0 \times 10^{-10} \text{ m}^2/\text{s}$ vs. $D_{\text{MeOH} (\text{water})} = 1.58 \times 10^{-10} \text{ m}^2/\text{s}$), this layer of Nafion can reduce the rate of the methanol diffusion to cathode catalyst.

Another method to alleviate fuel crossover by reducing the mass transport is using low fuel concentration. With this method, the driving force for fuel diffusion decreases. The combination of the two methods allows an operation over a wide range of fuel concentrations. The maximum power density can then be improved by a factor of 2.5. The peak power density of a single cell operating at 80 °C with

1 M of methanol and O_2 supply and without a separator and Nafion on the cathode is 28 mW/cm^2 . Adding either Nafion on cathode or a separator enhances the maximum power density to more than 40 mW/cm^2 . Exploiting both means, the peak power density reaches 70 mW/cm^2 .

Fuel can diffuse through the fuel-electrolyte interface to reach the cathode, decreasing the performance. To address this issue, Whipple et al. [56] developed a fuel (methanol) tolerant catalyst for the oxygen electroreduction reactions. For this purpose, ruthenium-selenium chalcogenides (Ru_xSe_y) improved the cathode performance in the presence of 1 to 7 M methanol by as much as 30-60 %. The improvement of oxygen transport at the cathode side due to the change in solubility and diffusivity can be considered as a possible explanation for the observed increase in performance of Ru_xSe_y -based cathode. However, the absolute performance of the cell with Ru_xSe_y is lower than a cell with Pt cathode by a factor of 4 ($\sim 4 \text{ mW/cm}^2$ vs. $\sim 16 \text{ mW/cm}^2$). In this concept, fuel crossover is not a concern anymore and the electrolyte can be eliminated as a separating stream. The elimination of electrolyte can reduce the size, weight and the complexity of the whole fuel cell. A much higher fuel concentration can be used, so that the energy

Figure 2.8 Different approaches of controlling inter-diffusion zone; (a) Using cross-flow configuration with electrolyte stream to control diffusive mixing at the fuel-oxidant interface, reproduced after [74]; (b) Implementation a nonporous separator and coated Nafion layer to control fuel crossover at the interface of co-laminar flows and over cathode side, reproduced after [55].

density of the cell can be improved.

2.7 Gas Bubble Formation

Since membraneless LFFCs exploit the laminar flow regime at very low Reynolds numbers, the interface of co-laminar streams are not affected by the velocity fluctuations. But other factors including bubble generation within the channel may disturb the interface leading to uncontrolled mixing and performance degradation.

In addition to controlling the flow rate of two streams to reduce diffusive mixing and fuel crossover, several methods have been proposed to stabilize the liquid-liquid interface such as using a grooved microchannel [32], introducing a third electrolyte stream between oxidant and fuel streams [73], using porous separator at the liquid-liquid interface [55], optimizing the channel geometry and tailoring the electrode geometry [62, 72, 76].

Oxygen generation occurs in membraneless LFFC operating on H_2O_2 due to the spontaneous decomposition of H_2O_2 [77]. Parasitic oxidation of H_2O_2 at the cathode of a membraneless LFFC running on formic acid also generate bubbles [32]. In addition to oxygen generation, carbon dioxide is generated from oxidation of formic acid and methanol [78]. Choban et al. [65] argued that the bubble formation, especially the formation of CO_2 bubble would degrade the performance of a membraneless LFFC. Bubbles generated in the channel reduce the performance by (i) decreasing the effective electrode area and (ii) the destruction of the liquid-liquid interface. Bubbles attach to the channel wall resulting in blockage. In addition, generation and detachment of bubbles and slug flow cause an intermittent flow field through the channel that can disturb the liquid-liquid interface [78]. In conclusion, crossover effects and the decrease of open-circuit

potential are the consequences of bubble generation. Furthermore, to conduct a valid numerical simulation of membraneless LFFC, bubble generation and the associated two-phase flow must be taken into account.

Shyu et al. [78] visualized the oxygen bubbles produced due to the decomposition of hydrogen peroxide in a microreactor with platinum-deposited electrodes. Two streams of water and hydrogen peroxide were introduced into a Y-shaped microchannel. Evaluation of the mixing index was used to examine the effect of bubbles on the concentration distribution of two streams.

Analysis of mixing and flow visualization revealed that bubble generation depends on the flow rate, the solubility of the species, the concentration of the species and the cell current density. Generation rate of gases such as oxygen or carbon dioxide depends directly on the cell current density. The produced gas (solute) can dissolve in the medium (solvent). The solubility of carbon dioxide is 90 ml in 100 ml of water at room temperature. On the one hand, CO₂ formed in the channel dissolves in the flowing stream and is carried away from the system [65]. On the other hand, gas bubbles can appear in the stream if the liquid is saturated. In this case, a membraneless LFFC running at low flow rates is more prone to bubble generation.

Oxygen solubility in water (0.91 mg/100 mL) is much smaller than that of carbon dioxide (178.2 mg/100 mL). Thus, the presence of O₂ bubbles in a microchannel affect the performance more significantly. Kjeang et al. [32] fabricated a membraneless LFFC using a grooved microchannel in PDMS running on formic acid and hydrogen peroxide as fuel and oxidant, respectively. The aim of using the grooved microchannels shown in Figure 2.1(e) is to capture the oxygen bubbles formed by the parasitic electrochemical reactions over a cathode

while stabilizing the co-laminar flow. Li et al [39] reported that the O₂ bubbles generated from the parasitic decomposition of H₂O₂ result in fluctuation of the open-circuit potential. As a rule of thumb, the effect of gas solubility in both fuel and oxidant streams at a given flow rate must be taken into account to avoid bubble generation in a membraneless LFFC.

2.8 Fuel, Oxidant and Electrolytes

2.8.1 Fuel Types

Membraneless LFFCs have a wide range of fuel options. The available fuels are hydrogen (H₂) [36, 41, 79], methanol (CH₃OH) [29, 50], ethanol (C₂H₅OH) [54] formic acid [40, 73], hydrogen peroxide (H₂O₂) [77] vanadium redox species [17, 80], and sodium borohydride (NaBH₄) [54] and hydrazine (N₂H₄) [54].

Among the aqueous fuels, formic acid and methanol with respective energy densities of 2.08 kWh/l and 4.69 kWh/l attracted more attention for use in membraneless LFFC due to the ease of access and the well-studied electrocatalysis. A formic acid/O₂ fuel cell has a high theoretical electromotive force of 1.45 V, while the corresponding value of methanol is 1.2 V.

Cohen et al. [40] tested a membraneless LFFC running on formic acid as fuel with platinum as catalyst and dissolved oxygen as oxidant:

Using formic acid as fuel can provide a large open-circuit potential and high electrochemical efficiency [40]. The main disadvantage of formic acid is carbon monoxide poisoning of the Pt-based catalyst.

Usually, vanadium redox couples dissolved in a supporting electrolyte such as sulfuric acid, V^{2+}/V^{3+} as anolyte and VO_2^+/VO^{2+} as catholyte are used to form all-vanadium fuel/oxidant system for membraneless LFFCs [17, 30, 48, 74]. A membraneless LFFC can follow anodic and cathodic redox reactions [48]:

The advantages of this redox combination for microfluidic fuel cells are [24, 48]: (i) in providing well-balanced electrochemical half-cells in terms of reaction rates and transport characteristics, (ii) high solubility and relatively high redox concentration up to 5.4 M, (iii) high open-circuit voltage (up to ~1.7 V at uniform pH) due to the presence of large difference in formal redox potentials, and (iv) utilization of bare carbon electrodes without precious metal catalyst to facilitate the reactions.

The energy density of a vanadium redox fuel cell is limited by the solubility of the vanadium redox species. To address this situation, a new alkaline microfluidic fuel cell was demonstrated by Kjeang et al. [33] using formic acid and hypochlorite oxidant. The reactant solutions were obtained from formic and sodium hypochlorite. Both are available and stable as highly concentrated liquids, leading to a fuel cell system with high overall energy density. Formate ($HCOO^-$) oxidation and hypochlorite reduction were established in alkaline media on porous Pd and Au electrodes, respectively. The results indicate the rapid reaction kinetics at low overpotentials while preventing gaseous CO_2 formation by carbonate absorption.

Brushett et al. [54] utilized 3 M hydrazine as fuel with 0.5 M of sulfuric acid as electrolyte in an air-breathing flow architecture. For this hydrazine

membraneless LFFC, a maximum power density of 80 mW/cm^2 was achieved at room temperature. The anode catalyst loading was 1 mg/cm^2 supported Pt. The flow rate of fuel and electrolyte were 0.3 ml/min . Moreover, with the same operating conditions, hydrazine was tested with oxygen flow rate of 50 sccm instead of quiescent air. No considerable improvement was observed for the peak power density and maximum current density indicating that this membraneless LFFC configuration is not restricted by oxygen transport.

The direct hydrazine acidic membraneless LFFC can be a promising micro-scale power source for applications where the safety is not a major concern. The theoretical open-circuit potential of a hydrazine/ O_2 fuel cell is 1.56 V . In addition, the end products of complete electrooxidation of hydrazine/ O_2 are nitrogen gas and water which make the hydrazine fuel cell an eco-friendly zero-emission energy convertor [54]. Also, Brushett et al. [54] used 1 M sodium borohydride in 1 M KOH as fuel on Pt anode. Sodium borohydride with energy density of 9295 Wh/kg is unstable in acidic media, but highly stable in alkaline media. A peak power density of 101 mW/cm^2 was recorded for both fuel and electrolyte streams (1 M KOH) flow at 0.3 ml/min with air-breathing cathode. This high performance is mainly credited to the improved electrocatalytic activity of Pt towards the oxidation of the borohydride anions.

2.8.2 Oxidant Types

Oxidant for a microfluidic fuel cell can be dissolved oxygen in aqueous form [29, 39, 51, 65], air [18, 49, 50, 54, 56], hydrogen peroxide [32, 77], vanadium redox species [17, 30, 80], potassium permanganate [47, 73], and sodium hypochlorite [33].

Basically, the cathodic half-cell electrokinetics is slower than the anodic one. The oxygen reduction reaction (ORR) is sluggish. Completion of ORR requires many individual steps and significant molecular reorganization, so the majority of activation overvoltage loss takes place at the cathode. At standard ambient temperature and pressure (298.15 K, 1 atm), the exchange current densities for oxygen reduction reaction (ORR) on Pt is six orders of magnitude lower than that of the hydrogen oxidation reaction (HOR). When the dissolved oxygen is used as oxidant, the slow electrokinetic reactions in cathode are coupled with low oxygen concentration resulting in a low power density. Alternative oxidants soluble at higher concentration than dissolved oxygen can be used for improving the mass transport limitation of dissolved oxygen in electrolyte.

In general, fuel cells using liquid oxidants have more power output. Chohan et al. [65] replaced oxygen saturated in 0.5 M sulfuric acid by 0.144 M potassium permanganate as oxidant and used 2.1 M formic acid as fuel. The results showed that the cell operation using potassium permanganate produced a current density with one order of magnitude higher due to the higher solubility of potassium permanganate in aqueous media [52].

Li et al. [39], utilized saturated oxygen in 0.1 M H_2SO_4 solution as oxidant with 0.5 M HCOOH in 0.1 M H_2SO_4 solution as fuel. The relatively low maximum power density of 0.58 mWcm^{-2} was caused by insufficient supply of oxygen from oxidant stream to the cathode.

Gaseous air was also used as oxidant in air-breathing microfluidic fuel cells [18, 49, 50]. Since the concentration of oxygen in air ($0.2 \text{ cm}^2/\text{s}$) is 4 orders of magnitude higher than in aqueous media ($2 \times 10^{-5} \text{ cm}^2/\text{s}$) [49], the air cathode designs can provide higher maximum power density and power output.

2.8.3 Electrolytes

In most membraneless LFFC designs, fuel and oxidant are dissolved in electrolyte and then delivered into the channel using syringe pumps. The main reason for adding electrolyte to the streams is to enhance the ionic conduction and to decrease the Ohmic losses between the anode and the cathode. Adding sulfuric acid to both streams in a membraneless LFFC provides a source of protons closer to the cathode. Because of the proton consumption at the cathode, a gradient of protons is maintained [65]. Experimental results reported by Choban et al. [65] revealed that using 0.5 M sulfuric acid as a supporting electrolyte can provide a maximum current density of 0.9 mW/cm^2 . For comparison, the maximum current density of the LFFC with water as electrolyte was just 0.2 mW/cm^2 at the maximum volumetric flow rate of 0.8 ml/min .

Lack of the membrane allows the cell to operate in both acidic and alkaline media, as well as in “mixed-media” where the cathode is in acidic and anode is in alkali media, or vice versa [29]. This flexible choice of media allows the designer to tailor the composition of cathode and anode streams individually, and to optimize the individual electrode kinetics as well as the overall cell potential [29].

The pH of the electrolyte affects the reaction kinetics at the individual electrodes and electrode potential [29]. The electrolyte is typically a strong acid or a strong base. For instance, sulfuric acid or potassium hydroxide have highly mobile hydronium or hydroxide ions, respectively [24]. Typically, operation of a fuel cell in alkaline media can lead to electrooxidation of the catalyst-poisoning carbon monoxide species on the anode improving the kinetics of ORR at the cathode [29]. However, due to the potential of carbonate formation resulting in clogging the membrane, the long-term stability of membrane-based

fuel cells is restricted and limits the use of these alkali-compatible membranes for liquid fuel cell operations [29].

Bruhsett et al. [54] examined the performance of air-breathing membraneless LFFC operated on ethanol and methanol under acidic (H_2SO_4) and alkaline (KOH) conditions. Methanol and ethanol showed improved open circuit potential and maximum power density in alkaline media (1.2 V and 0.7 V, 17.2 mW/cm^2 and 12.1 mW/cm^2) compared to acidic media (0.93 V and 0.41 V, 11.8 mW/cm^2 and 1.9 mW/cm^2). The improved performance in alkaline media was caused by the enhanced kinetics of alcohol oxidation and oxygen reduction.

Choban et al. [29] investigated the influence of acidic (H_2SO_4), alkaline (KOH) and acidic/alkaline media on the cell potential and power output of a membraneless LFFC running on 1 M methanol and dissolved oxygen. The results indicate that the process in both acidic and alkaline media was cathode-limited, which can be attributed to the low oxygen concentration in the solution. The oxygen solubility in acidic media was about 1 mM, while the oxygen solubility in alkaline media was approximately 25% lower, resulting in an earlier drop of the I-V curve [29]. There is no issue with carbonate formation due to the immediate removal of any formed carbonates from the system by the flowing streams.

A maximum theoretical OCP is 0.38 V expected for an acidic anode stream and an alkaline cathode stream. However, an OCP of less than 0.1 V was observed due to the overpotentials on the cathode and anode. In other words, the energy liberated in the methanol oxidation and oxygen reduction reactions is mostly used by water ionization reaction. In this configuration, the electrolytic reaction combined with a galvanic reaction is incapable of producing a large amount of energy [29].

In the case of alkaline anode and acidic cathode, the combination of two galvanic reactions yields a high theoretical OCP of 2.04 V. However, the practical OCP is only 1.4 V due to the slow kinetics of oxygen reduction and methanol oxidation. The power density of mixed media is higher than those obtained for all-acidic and all-alkaline membraneless LFFCs.

Most of the observed additional power density for the mixed media configuration is supplied by the electrochemical acid-base neutralization reaction where protons are reduced at the cathode and hydroxide ions are consumed at the anode. Therefore, the consumption of H_2SO_4 and KOH must be taken into account while comparing the different membraneless LFFC configurations.

While the cell is running under alkaline anode with acidic cathode conditions, both OH^- and H^+ are consumed at the anode and cathode at a rate of six ions for each molecule of methanol. Based on the reaction of 1 M of methanol with ambient oxygen, consuming six equivalents of H_2SO_4 and KOH , the maximum theoretical energy density is 495 Wh/kg. This value is much lower than the theoretical value of 6000 Wh/kg for the all-alkaline and all-acidic LFFC where only methanol is consumed [29].

Hasegawa et al. [77] utilized the mixed media approach to operate a microfluidic fuel cell on hydrogen peroxide as both fuel and oxidant, in alkaline (NaOH) and acidic (H_2SO_4) media, respectively. This design produced a relatively high power density up to 23 mW/cm². The drawback of this design is the spontaneous decomposition of hydrogen peroxide on the cathode and the associated generation of oxygen bubbles that may disturb the co-laminar flow interface.

The overall reaction for this design is:

which involves the disproportionate reaction of H_2O_2 together with the combination of H^+ and OH^- ions. SO_4^{2-} ion neutralizes Na^+ ion electrically at the acidic/alkaline bipolar electrolyte interface. Consequently, the products of this fuel cell type are water, oxygen, and salt.

2.9 Challenges and Opportunities for Further Developments

Amongst the different designs of membraneless LFFCs available in the literature, membraneless LFFC with air-breathing cathode seems to be a promising design for practical operations. Since oxygen is supplied through a gas diffusion electrode, optimization activities can be focused on the fuel stream. Almost all reported designs of air-breathing microfluidic fuel cells run on high flow rate of fuel and electrolyte to increase the maximum power density while fuel utilization per single pass drops. A fuel recirculation scheme must be integrated with the fuel cell to increase the overall energy density. This scheme may add complexity to the system design. Investigation on long-term performance has been ignored in the literature. Current designs suffer from incompatibility with stacking schemes for making interconnected cells. These issues must be addressed for practical applications. In current designs of all microfluidic fuel cells, three reservoirs are needed to contain fuel, oxidant or electrolyte as well as waste. As space is a design constrain, integration of these reservoirs with the fuel cell system would add more complexity to the design and make the whole structure bulky and difficult to integrate with other micro devices. Therefore developing a one-compartment fuel cell with selective electrodes running on a single reactant as both fuel and oxidant is of great importance and interest. Such a fuel cell does not need continuous pumping of reactants streams to keep the fuel separated from the

oxidant. Auxiliary components can be kept minimal. The whole fuel cell can be fabricated in a very compact and cost-effective way, making it easy to be integrated with a power consumer

In order to address the above mentioned issues, the scope of this thesis is organized into the following activities:

- In Chapter 4, a numerical simulation of anode and cathode was carried out to better understand the interaction between mass transport and electrochemical processes within the cell. The model shows that low fuel utilization is a major issue that must be addressed. The fuel utilization rate can be improved by optimizing the flow architecture of the fuel cell.
- Chapter 5 reports the improvement of fuel utilization per single pass in an air-breathing microfluidic fuel cell with flow-through anode. Higher performance compared to a flow-over design was achieved by paying careful attention on the coupled mass transport to reactive sites and the electrochemical kinetics. As fuel utilization increases, mass transport to anode reactive sites could be affected by the formation of CO_2 bubbles, a by-product of formic acid electrooxidation.
- In Chapter 6, a novel design of air-breathing microfluidic fuel cell was fabricated and characterized to improve mass transport to the anode site and consequently the overall cell performance. Ohmic losses are decreased by reducing the spacing between the electrodes. This design of air-breathing microfluidic fuel cell can provide a suitable platform for the realization of interconnected cells for a larger amount of power.
- In Chapter 7, the proof-of-concept of an one-compartment fuel cell running on hydrogen peroxide as both fuel and oxidant was developed. The fuel cell

shows a superior performance compared to other one-compartment membraneless fuel cells reported in the literature. This design can open a new avenue for further development of micro fuel cells for on-chip power generation.

Chapter 3 Experimental Methods

Abstract

This chapter describes experimental procedure used for characterizing the performance of different microfluidic fuel cells reported in chapters 4 to 6. For all experiments, different concentrations of formic acid containing 0.5 M sulfuric acid as supporting electrolyte and a stream of 0.5 M sulfuric acid were used.

3.1 Electrochemical Reactions

The generation of electricity in a LFFC follows electrochemical reactions over electrodes. For all experiments described in chapters 4 to 6, different concentrations of formic acid (0.5 M, 1 M and 3 M) containing 0.5 M sulfuric acid as supporting electrolyte were used as fuel and a separate stream of 0.5 M H₂SO₄ was introduced to the fluidic channel to separate the fuel stream from the cathode side.

Introducing the electrolyte stream into the channel has two main functions. The first function is to avoid the mixed potential due to the oxidation of formic acid at the cathode that can dramatically reduce the performance [56]. The second function is the prevention of catalyst poisoning due to formic acid oxidation at the Pt-supported cathode. Both catalyst poisoning and mixed potential on the cathode are the consequences of fuel diffusion from the anode to the cathode. Fuel diffusion can be minimized by the fine adjustment of fuel-electrolyte interface and their flow rates.

Formic acid has a lower energy density of 2104 Wh/l as compared to methanol with an energy density of 4900 Wh/l [81]. However, formic acid has faster electrooxidation kinetics at room temperature [13]. Formic acid is also a strong electrolyte, so this fuel can enhance proton transport at the anode side, and it is safe for the environment [82].

The electro-oxidation of formic acid on Pt and selected Pt-group metal surfaces is a dual pathway mechanism [82]. The first pathway is via dehydrogenation reaction which is the direct and favorite path for generating active species of H⁺ and releases electrons:

The second reaction pathway is via dehydration. Absorbed CO is produced as a poisoning intermediate which can block the active sites for direct pathway:

Adsorbed OH groups in step (3.3) oxidize the adsorbed CO intermediate into the gaseous CO₂ end product in step (3.4). Within the potential range of interest for fuel cell, OH groups are not readily adsorbed onto Pt. Consequently dehydrogenation pathway is the desired reaction within the potential range of interest [82]. Palladium (Pd) has the tendency of breaking the O-H bonds of formic acid over the whole potential region. As a result, oxidation of formic acid on Pd surfaces mostly proceeds through the dehydrogenation reaction step [81]. Pd is added to Pt to enhance reaction of Equation (3.1), while Ruthenium (Ru) addition is expected to enhance the reaction of Equation (3.4) [83].

Oxygen is supplied through the gas-diffusion cathode from the ambient air. This catalytic oxygen reduction reaction is a multi-electron process with a number of elementary steps. Without considering different reaction intermediates, oxygen reduction reaction (ORR) occurs as:

3.2 Electrode Fabrication

In order to fabricate the anode, catalyst ink was prepared using high-surface-area Pd black particles (99.9% metal basis) from Alfa-Aesar or Pt-Ru 20:20 atom. wt% alloy (E-TEK) were mixed with carbon nanoparticles (Vulcan X72) with a

loading of 1 mg/cm^2 to improve the dispersion of Pd particles. Nafion solution with a loading of 3 mg/cm^2 (for Pd) or 1.5 mg/cm^2 (for Pt-Ru) was used as a binder. To have a low-viscosity ink, isopropanol was added to the mixture followed by ultrasound sonication for 1 hour.

The catalyst ink was spread manually over a $10 \times 10 \text{ cm}^2$ piece of plain Toray carbon paper with a porosity of 78% [84] and a typical measured thickness of $280 \text{ }\mu\text{m}$. The carbon paper was then dried under a fume hood for 20 minutes and subsequently kept in an oven at a temperature of $80 \text{ }^\circ\text{C}$ for 1 hour. To make electrode strips, carbon paper was cut in the required size to work as the anode.

Cathodes were fabricated using plain carbon paper. For the experiment described in chapter 4, the carbon paper was dipped in a 5% polytetrafluoroethylene (PTFE) solution for 2 minutes. After drying at room temperature, the paper was baked at 250°C for 30 min and at 350°C for another 30 min to achieve a hydrophobic surface. The PTFE coating avoids liquid leakage from the channel through the porous carbon paper into the environment. The immersion of carbon paper in the PTFE solution decreases its porosity, depending on the concentration of the PTFE solution [84]. For 5% PTFE solution, the porosity reduction is less than 1% [84].

The cathode has a double-layer catalyst loading [50]. The first layer contains 0.3 mg/cm^2 platinum nanoparticles supported on Vulcan XC 72 (Alfa-Aesar). The second layer, which is exposed directly to the electrolyte stream of 0.5 M sulfuric acid, has a loading of 2 mg/cm^2 platinum and approximately 0.1 mg/cm^2 Nafion.

For the experiments of Chapters 5 and 6, commercial carbon-fiber-based cathode (Alfa-Aesar) was used to provide consistent results. Teflon[®] content of

the cathode is high enough to prevent leakage from the channel through the gas-diffusion electrode.

3.3 Experimental Conditions

The flow rate of the fuel and the electrolyte streams were kept constant at a fixed fuel-to-electrolyte ratio of 1:1. Fuel cells were tested with fuel flow rates of 10, 20, 50, 100, 200 and 500 $\mu\text{l}/\text{min}$. Both fuel and electrolyte streams were delivered by a syringe pump (KD Scientific). To receive repeatable results, the following procedure was applied. Prior to running the experiment at a given flow rate, the syringe pump was driven for a fixed period of time, from 5 minutes at 200 $\mu\text{l}/\text{min}$ to 20 minutes at 20 $\mu\text{l}/\text{min}$. This step warrants that flow conditions including liquid-liquid interface and velocity field inside the cell were stabilized. In addition, this step ensures that the syringe pump can reach the steady-state operational conditions prior to the experiment. A potential scanning rate of 5 mV/s with a potential step of 0.01 V was used.

The characterization of the fuel cells was carried out at room temperature of 25°C. The current at different cell potentials was measured with an electric load system (PGSTAT 302 with GPES Manager as interface software), Figure 3.1.

To evaluate the combined Ohmic cell resistance, electrochemical impedance spectroscopy (EIS) was carried out at the open-circuit voltage (OCV) and a flow rate of 200 $\mu\text{l}/\text{min}$. Frequency range of EIS was from 0.1 Hz to 100 kHz with an AC amplitude of 10 mVrms. The intercept of high-frequency impedance spectrum and the real axis indicates the total cell resistance. In OCV condition, there is no disturbance in the channel. For instance, bubble generation due to current generation may alter the lamination of two streams or change the cross-sectional area of charge transport from anode to cathode. For all fabricated cells, OCV was

Figure 3.1. A schematic of the experimental setup.

monitored for 10 to 20 minutes before each experiment to ensure the stable liquid-liquid interface in the channel.

Chapter 4 Numerical Simulation of an Air-breathing Microfluidic Fuel Cell*

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Abstract

In this chapter, numerical simulation was carried out to provide insight into the coupled electrochemical and mass transport phenomenon in a microfluidic fuel cell. In order to have a quantitative understanding of the experimental results, a three-dimensional model based on finite element method (FEM) was established. The model solves the coupled electrochemical reactions and transport phenomena within the fuel cell under the same experimental conditions and with the same geometry. The results obtained from this simulation provide an avenue for further optimization measures.

4.1 Fuel Cell Design and Fabrication

Because of the laminar nature of the reactant stream in the channel, flow architecture and the interaction of reactant-electrode play an important role on the overall cell performance. In order to improve the overall performance and to increase fuel utilization for electricity generation, the flow architecture and the associated limiting transport properties within an air-breathing microfluidic fuel cell must be identified. In addition, modeling of microfluidic fuel cells reduces the time and effort for design, fabrication and characterization of new microfluidic fuel cells. To have a quantitative understanding of the experimental results, a three-dimensional model based on Finite Element Method (FEM) using the commercial software (COMSOL Multiphysics) was established.

A microfluidic fuel cell was fabricated and characterized to validate the numerical simulation, Figure 4.1. In a T-shaped channel, fuel containing 1 M formic acid and 0.5 M sulfuric acid was introduced into the channel from the bottom inlet. Inlet of the electrolyte stream is on the top. The electrodes has a top-bottom arrangement. The model solves the coupled electrochemical reactions and transport phenomena within the fuel cell under the same experimental operating conditions with the same geometry. The channel width and length are 2 mm and 50 mm, respectively. The channel height of 0.9 mm was engraved in the PMMA sheet by adjusting the power and scanning speed of the laser machining system (Universal M-300 Laser Platform, Universal Laser Systems Inc., AZ, USA).

A piece of plain Toray carbon paper with a width of 2 mm and a length of 40 mm was placed at the bottom of the channel to work as the anode. The final active area of the anode measures 2 mm $\times$ 30 mm. The active area was coated

Figure 4.1 Schematic of the air-breathing microfluidic fuel cell: (a) Exploded view of the fuel cell; (b) Details of the assembled cell (not to scale).

with platinum-ruthenium (Pt-Ru) alloy nanoparticles working as an electrocatalyst with a total active electrode area of 0.6 cm².

A 1-mm thick PMMA sheet was cut by the same laser system to serve as the cover for the channel. This PMMA layer has a 2 mm × 30 mm slot to hold the cathode made of Toray carbon paper. The gas diffusion electrode (GDE) was assembled on the PMMA sheet using epoxy (Araldite, Huntsmann, USA). Before bonding the two PMMA sheets, both PMMA surfaces were mechanically treated by a piece of fine sand paper to improve the surface roughness for better adhesion. The two PMMA pieces were then bonded together using chloroform. Electrically conducting copper wires were attached to the electrodes using conductive silver epoxy (Chemtronics, USA). The electrodes were aligned and positioned to

Figure 4.2 Fabricated fuel cell: (a) Arrangement of inlets and outlet; (b) GDE and wires attached to the anode and cathode.

maintain the 0.6 cm^2 active surface area on both electrodes. The fuel and electrolyte inlets were cut by the laser system and have a diameter of 1.3 mm. A single outlet with a diameter of 2 mm was cut on the top layer. Fluidic interconnects were glued to the cell using epoxy adhesive. Tubing with an inner diameter of 0.062 inch and an outer diameter of 0.125 inch (Cole-Parmer) was used for delivering the fuel, electrolyte and waste. After the final assembly, the LFFC was tested for leakage with de-ionized (DI) water. Figure 4.2 depicts the assembled LFFC.

4.2 Model Formulation and Theory

The model developed in this chapter does not aim to fully describe all transport phenomena and electrochemical reactions within the fuel cell. A complete simulation of all physicochemical interactions in a microfluidic fuel cell is highly complex with a large-degree of non-linearity [85]. In order to manage the problem, some simplifications are needed. The focus of this numerical simulation is to capture the impact of key transport phenomena on the cell performance. New

solutions for performance improvement can be obtained with better understanding of the cell operation.

Key assumptions made for this simulation are listed as follow:

(i) For both fuel and electrolyte streams, incompressible fluid flow is assumed. Effect of gravity is neglected.

(ii) Isothermal and steady state conditions are considered. Since liquid velocities are very moderate, internal heating because of viscous dissipation is ignored. Therefore, an isothermal system is assumed [71].

(iii) Physical properties of the electrodes and electrolyte are homogeneous.

Other assumptions will be described in details as required in the following sections.

4.3 Hydrodynamic Equations

Electrical double layer (EDL) is formed at the interface of the electrodes and the electrolyte. EDL consists of the inner Stern layer and the outer diffuse layer. EDL has a critical role in charge transfer across the electrode-electrolyte interface [86]. Because of the potential gradient across the electrodes, electric body force (EBF) is created resulting in electroosmotic pressure [87]. Sprague et al. [86] showed that EBF effects on ion concentration distribution and velocity field in a microfluidic fuel cell is negligible. Consequently, the effect of EBF is not considered in the Navier-Stokes equation and electroneutrality condition for the whole fluid is assumed. Simulation of ionic migration is neglected because of the high concentration of the acid supporting electrolyte [85].

Figure 4.3. Schematic of the computational domain

To solve the flow field in the channel and through the porous anode, continuity and Navier–Stokes equations are solved for the steady-state and laminar flow condition ($Re < 10$):

$$\nabla \cdot (\rho \mathbf{u}) = 0 \quad (4.1)$$

$$\nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\frac{1}{\rho} \nabla p + \nabla \cdot (\mu \nabla \mathbf{u}) \quad (4.2)$$

where p is the static pressure, $\mathbf{u}$ is the velocity vector, ρ is the fluid density, and μ is the kinematic viscosity. The system is considered as an isothermal system. The viscous dissipation due to the low liquid velocities through the channel ($u < 1$ cm/s) can be ignored. Since the anolyte and electrolyte are dilute solutions, the input density of anolyte and electrolyte are taken as that of water. Density of a solution of 1 M HCOOH containing 0.5 M H₂SO₄, used as fuel is 1031 kg/m³ while the density of a solution of 0.5 M H₂SO₄ used as electrolyte stream is 1028 kg/m³.

To solve the flow distribution in the porous media, Darcy's law is used [88]:

$$\mathbf{u} = -\frac{k}{\mu} \nabla p \quad (4.3)$$

where k is the intrinsic permeability of the porous media. Intrinsic permeability is known as the permeability of a single phase flow. Intrinsic permeability is

independent of the nature of the fluid, and depends on the structure of the porous medium [88]. Darcy's law is based on the homogenization of the porous medium and fluid into one single medium [89]. So, a detailed geometrical description of the pores is not required to solve the Darcy's model. According to equation (4.3), a pressure gradient is the driving force for flow in the porous media.

Since a horizontal liquid-liquid interface is established in the channel, effects of gravity-induced reorientation on hydrodynamics are neglected [90].

4.4 Mass Transport and Electrochemical Model

Formic acid is oxidized at the anode, which is implemented on the bottom wall of the channel. The electrooxidation of formic acid to carbon dioxide (CO_2) on a metal surface is assumed to take place via a dual path mechanism [81]. In the current model, the direct pathway is assumed to be the dominant oxidation of formic acid.

The catalytic oxygen reduction reaction (ORR) is a multi-electron process with a number of elementary steps, entailing different reaction intermediates [91]. Without considering the reaction intermediates, the oxygen reduction at the cathode is considered.

Anode and cathode are both made of porous carbon paper covered by a thin layer of catalyst particles. The catalyst layer is treated in the model as a boundary. The corresponding electrochemical reactions take place over this boundary. So the effect of these reactions on the species concentration appears as the source term S in the equation of conservation of species:

$$\nabla \cdot (-D_i \nabla C_i + C_i \vec{u}) = S_i \quad (4.4)$$

where S_i is the net rate of change of species “ i ” by electrochemical reactions over anode and cathode, and represents the rate of consumed species per cubic meter. D_i is the diffusion coefficient of species “ i ” in the corresponding media referring to formic acid at the anode and oxygen at the cathode. The value of D for anodic and cathodic reactions are considered as formic acid diffusivity in aqueous media (water) and oxygen diffusivity through gas diffusion electrode (GDE) and the aqueous media of electrolyte respectively, C is the concentration of corresponding species at the anode and the cathode.

The rates of formic acid electrooxidation at the anode and electroreduction of oxygen at the cathode are given by:

$$S_i = \left(\frac{j_0}{n_i F} \right) \left(\frac{C_i}{C_{i,ref}} \right)^{\beta_i} \left[\exp\left(\frac{\alpha_a F \eta}{RT} \right) - \exp\left(-\frac{\alpha_c F \eta}{RT} \right) \right] \quad (4.5)$$

where j_0 is the exchange current density at the reference reactant concentration $C_{i,ref}$, β_i is the reaction order of species “ i ” for the elementary charge transfer step. Since the rate determining step is a first-order reaction, $\beta = 1$ is chosen [71], α_a and α_c are the anodic and cathodic charge transfer coefficients, R is the universal gas constant and T is the operating temperature and is considered as a constant parameter, F is the Faraday’s constant, and η is the activation overpotential.

Oxygen from atmosphere diffuses through the GDE to reach the catalyst layer. Therefore, diffusion transport through the GDE is considered in the model. To determine the oxygen concentration through the GDE, Equations (4.4) and (4.5) are solved with input values and appropriate boundary conditions as listed in Tables 4.1 and 4.2. On the catalytic surface, only the normal flux to the surface contributes to power output of the cell [60] and is given by:

$$\vec{n} \cdot \nabla \cdot (-D_{ij} \nabla C_i + C_i \vec{u}) = S_i \quad (4.6)$$

Due to the porous nature of cathode and anode, the binary diffusion coefficients utilized in the porous media are corrected for the porosity (ε) and tortuosity (τ) of the media as follows [92]:

$$D_{ij}^{eff} = D_{ij} \frac{\varepsilon}{\tau} \quad (4.7)$$

The released protons from hydrogen oxidation at the anode diffuse across the channel to react with oxygen. Proton transfer to the cathode side is facilitated by the potential gradient between the electrodes [55]. In addition to proton diffusion to the cathode, formic acid can diffuse and reach the cathode at low flow rates. Formic acid adjacent to the cathode catalyst can be oxidized decreasing the cathode voltage due to the mixed potential. In this model, the effect of fuel crossover on the cathode and the simulation of the waste products are not considered.

4.5 Boundary Conditions

To determine the flow field through the channel, the fuel-to-electrolyte flow rate ratio of 1:1 is chosen while the outlet boundary condition is set on zero pressure. The inlet velocities are set in the model according to the experimental flow rates mentioned in Chapter 3. Three different flow rates $Q_1=500 \mu\text{l/min}$, $Q_2=100 \mu\text{l/min}$ and $Q_3=10 \mu\text{l/min}$ with the respective inlet velocity of 6, 1.2 and 0.12 mm/s were used in the simulation.

Formic acid with a concentration of 1 M is set at the inlet as anolyte stream for all simulations, while the concentration of formic acid at the inlet of electrolyte stream is set to be zero. The outlet condition is set as convective mass transport.

Table 4.1 Constants and parameters used in the numerical simulation

Parameter	Description	Values	Units
$C_{0, HCOOH}$	Reference concentration of formic acid	500	mol m^{-3}
C_{0, O_2}	Reference concentration of oxygen	85	mol m^{-3}
C_{0, O_2}	Reference concentration of oxygen	85	mol m^{-3}
$D_{O_2(water)}$	Diffusivity of oxygen in water	2.1×10^{-9}	$\text{m}^2 \text{s}^{-1}$
$D_{O_2(air)}$	Diffusivity of oxygen in air	2.1×10^{-5}	$\text{m}^2 \text{s}^{-1}$
D_{HCOOH}	Diffusivity of formic acid as anolyte	2.546×10^{-9}	$\text{m}^2 \text{s}^{-1}$
$D_{O_2(water)}$	Diffusivity of oxygen in water	2.1×10^{-9}	$\text{m}^2 \text{s}^{-1}$
$D_{O_2(air)}$	Diffusivity of oxygen in air	2.1×10^{-5}	$\text{m}^2 \text{s}^{-1}$
n_a	Number of transferred electrons at anode	2	--
n_c	Number of transferred electrons at cathode	4	--
F	Faraday's constant	96485	C
j_{0a}	Exchange current density at anode	600	A m^{-2}
j_{0c}	Exchange current density at anode	5×10^{-6}	A m^{-2}
k	In-plane permeability of carbon paper	1×10^{-12}	m^2
K	Electrical conductivity of electrodes	300	$(\Omega \text{ m})^{-1}$
R	Universal gas constant	8.314	$\text{J mol}^{-1} \text{K}^{-1}$
T	Temperature	298	K
ε	Porosity of carbon paper used as GDE and anode	0.7	--
μ	Viscosity	10^{-3}	$\text{kg m}^{-1} \text{s}^{-1}$
ρ	Density of anolyte and electrolyte stream	1000	kg m^{-3}
τ	Tortuosity of carbon paper	3	--

Table 4.2 Boundary conditions used for hydrodynamic and electrochemical reactions

Boundary conditions to solve Equations (4.1) and (4.2)

 $u = (0, u_0)$ where u_0 is the inlet velocity (0.006, 0.0012, 0.00012 m/s)

 $u = (0, 0)$ at the walls

 $p = 0$ at the outlet (gauge pressure)

Boundary conditions to solve Equation (4.4) for anode and cathode reactions:

 $C = C_0$ at the inlet of anolyte stream

 $C = 0$ at the inlet of electrolyte stream

 $(-D\nabla C + C\mathbf{u}) \cdot \mathbf{n} = 0$ at the non-catalytic walls

 $(-D\nabla C) \cdot \mathbf{n} = 0$ at the outlet

The upper surface of the GDE is exposed to the ambient air and has an inlet concentration equal to the oxygen concentration of atmosphere. The bottom surface, working as the catalytic surface, has an inward flux of S_{O_2} determined by Equation (4.5). All parameters and the boundary conditions used in the numerical model are listed in Table 4.1 and Table 4.2. The critical values as input data are compiled from [60, 92-95].

4.5.1 Cathode and Anode Overpotentials

In order to solve Equation (4.5), species concentration and activation overpotential must be known for both electrodes. Furthermore, both voltage and the corresponding cell current density must be evaluated to plot the I - V curve. To

obtain the I - V curve, cell current is fixed and the corresponding voltage is calculated [96] by taking into account the different polarization losses based on the experimental data of the fabricated cell. The operating potential can be corrected from the ideal voltage, $E^o(T, P)$, by the various polarizations [28]:

$$E_{cell} = E^o(T, P) - \eta_{a,a} - |\eta_{a,c}| - \eta_r - \eta_{m,a} - |\eta_{m,c}| - \eta_x \quad (4.8)$$

where $E^o(T, P)$ is the theoretical equilibrium open-circuit potential of the cell, calculated from the Nernst equation. The variables $\eta_{a,a}$ and $\eta_{a,c}$ represent the activation overpotentials at the anode and the cathode. The Ohmic loss η_r occurs due to the resistance of the electrode materials and the electrical interconnects. The mass transfer or concentration polarization at the anode and the cathode are presented as $\eta_{m,a}$ and $\eta_{m,c}$, respectively. Crossover effect of fuel and oxidizer through the electrolyte or internal short circuits in the cell can be presented by η_x which is responsible for the departure of the theoretical equilibrium open-circuit potential from the Nernst equilibrium voltage.

Experimental data in Figure 4.4 show that there is no sharp voltage drop at high current densities for the given geometry and operation conditions. Therefore, mass transfer overpotential can be neglected to simplify the model. Effect of cross over (mixed potential) at anode and cathode sides and other parasitic losses can be taken into account in the open-circuit potential obtained from the experiment. In this case, Equation (4.8) can be considered as a semi-empirical equation and simplified to:

$$E_{cell} = E_{OCV} - \eta_{a,a} - |\eta_{a,c}| - \eta_r \quad (4.9)$$

Figure 4.4 Experimental polarization curves of the fuel cell running on three flow rates of formic acid.

where E_{OCV} is the experimental open-circuit voltage obtained from the I-V curve at a given flow rate, Figure 4.4. According to Equation (4.5), the current density is dependent on the concentration of the fuel and the oxidant. The species concentration can be calculated at a fixed current density with corresponding activation overpotential, $\eta_{a,a}$ and $\eta_{a,c}$, while the flow rate is known.

Figure 4.4 shows that the maximum current density (limiting current) is not determined by mass transfer overpotential, especially at high flow rates. The only exception is the flow rate of $Q_3=10 \mu\text{l}/\text{min}$ with a short drop observed at the limiting current. The main overpotential losses are mainly associated with activation and Ohmic losses. The Ohmic losses are attributed to the electrolyte proton conductivity and the resistance of the electrodes and external connections. Ohmic losses of the cell are calculated by:

$$\eta_r = i \cdot (R_{\text{electrolyte}} + R_{\text{external}}) \quad (4.10)$$

where $R_{electrolyte}$ is referred to the ionic resistance of the electrolyte. To have a good ionic conductivity across the channel from anode to cathode, 0.5 M sulfuric acid was mixed with 1 M of formic acid. The ionic conductivity of 0.5 M sulfuric acid is on the order of 0.2 S/cm [50]. Based on an anode to cathode spacing of 1.4 mm, a solution resistance of $0.7 \Omega \cdot \text{cm}^2$ was obtained. Cell potential minus activation and electrolyte losses results in the losses of external resistance ($R_{external}$). A value of 4.9Ω is considered for the external resistance, including the resistance of wiring and the electrical contacts.

To solve Equation (4.9), E_{ocv} and η_r were obtained from the experimental data while the anodic and cathodic activation overpotentials, $\eta_{a,a}$ and $\eta_{a,c}$ were taken from the simulation. The voltage calculated using Equation (4.9) is called $V_{cell, model}$.

Triangular mesh elements were used for the whole three-dimensional geometry in COMSOL. The total number of elements was 45170 which could produce mesh-independent results. Stationary non-linear solvent was used under the solver parameter menu with Direct (PARDISO out of core) system solver. This PARDISO out of core enables a computer to use the capacity of its RAM and hard disk to store data during computation. It means that more elements (finer mesh) could be used for computation.

The model was initially run to solve the Navier-Stokes equations. Then flow-field results were used to solve the mass transport and electrochemical equations. The stopping criterion for the iterations was set to 1×10^{-5} . The I-V curve was obtained by changing the cell current. The run time for each cell current varied between 8 to 10 minutes using a dual core Intel 4G-RAM.

4.6 Numerical Results and Conclusions

4.6.1 Polarization Losses in the Fuel Cell

Figure 4.5 shows the relative contribution of different polarization losses to the total polarization at a flow rate of 100 $\mu\text{l}/\text{min}$ or a corresponding inlet velocity of 1.2 mm/s. Cathodic overpotential has the largest contribution in voltage losses, especially at low current densities, because of the sluggish electroreduction of oxygen. Anodic loss is negligible compared to cathodic one. Ohmic loss is linear and increases with increasing current density. This figure indicates the activation overpotentials can be predicted in a good agreement with experimental data.

The discrepancy between the simulated and the experimental data occurs at high current densities. This discrepancy is mainly related to concentration losses. A mismatch between the simulated, Figure 4.6, and the experimental data occurred at limiting current densities, Figure 4.6. At low flow rates, the slow replenishment of depletion boundary layer over anode can lead to significant concentration polarization losses. A part of concentration polarization is attributed to the generation of local carbon dioxide bubbles over the anode because the electrooxidation of fuel was not taken into account in the model. These bubbles block the active sites of the anode for a short while and hinder fuel transport to the catalytic particles, but can be dissolved in the stream or washed away by the stream.

Figure 4.5 Contributions of different polarization losses at flow rate of 100 μl .

This model is selected as a platform to calculate the concentration distribution at different flow rates to gain a better understanding of the transport mechanism within the cell. The obtained results can be used to optimize the design in terms of electrode arrangement, flow architecture and the used materials.

Figure 4.6 Simulated voltage-current polarization curve of the fuel cell at different flow rates.

4.6.2 Concentration Distribution of Fuel

Equation (4.5) indicates that the concentration of fuel and oxidant plays an important role on the current density of a fuel cell. Good understanding of the species transport through the anode and the cathode can help to develop strategies for enhancing the performance and fuel utilization.

Figure 4.7 shows the concentration distribution of formic acid entering the channel at a concentration of 1000 mol/m^3 (1 M) for three flow rates of $Q_1=500 \text{ }\mu\text{l/min}$, $Q_2=100 \text{ }\mu\text{l/min}$, and $Q_3=10 \text{ }\mu\text{l/min}$ with the corresponding mean velocities of 6, 1.2 and 0.12 mm/s, respectively. The T-shaped cross-section of the channel is located at the x - y plane which cut through the center of the channel ($z = l/2w$) of a width w . After entering the channel, the concentration of the fuel decreases due to (i) diffusive mixing to the electrolyte stream, and (ii) the consumption at the anode.

At the highest flow rate of $Q_1=500 \text{ }\mu\text{l/min}$, the mixing region is limited to a very thin zone in the middle of the channel due to the high Peclet number ($Pe = 850$). At lower flow rates of $Q_2=100 \text{ }\mu\text{l/min}$ and $Q_3=10 \text{ }\mu\text{l/min}$ ($Pe = 170$ and 17), diffusion is apparent at the liquid-liquid interface. At $Q_3=10 \text{ }\mu\text{l/min}$, the fuel can diffuse across the electrolyte stream and reach the cathode side due to the low rate of replenishment.

Fuel is consumed over the anode forming a depletion boundary layer. At high flow rates, the depleted fuel is replenished rapidly by the supply of fresh fuel. As the feeding flow rate decreases, a zone with low fuel concentration is formed. At the flow rate of $Q_3=10 \text{ }\mu\text{l/min}$, the growth of the depletion boundary layer over anode is obvious. Since the anode is placed inside the channel from $x=1 \text{ cm}$ to

$x=4$ cm, the depletion boundary layer grows rapidly from $x=1$ cm indicating a low fuel concentration over the anode.

Figure 4.7 shows the concentration distribution of formic acid at the entrance ($x=1$ cm), centre ($x=2.5$ cm), as well as at the end of the anode electrode ($x=4$ cm) for the three flow rates. The anode was made of a piece of carbon paper with a thickness of $280\text{ }\mu\text{m}$. The upper surface of the anode exposed to the flow was covered with a catalyst layer. In Figure 4.8 to Figure 4.10, the location of catalyst layer is at $y = -600\text{ }\mu\text{m}$, while the liquid-liquid interface is indicated by $(0,0)$ at the height of the channel, Figure 4.3.

For all flow rates, the concentration of the fuel across the porous anode remains constant. At the vicinity of the catalyst layer, the concentration drops due to the fuel consumption. At the flow rate of $Q_1=500\text{ }\mu\text{l/min}$, the consumed fuel is replenished by the fuel stream, and the fuel concentration over the anode does not change significantly. In other words, the mass transport boundary layer remains thin over the electrode.

At the flow rate of $Q_2=100\text{ }\mu\text{l/min}$ and especially at the flow rate of

Figure 4.7 Concentration distribution of formic acid through the channel and over anode at the maximum current density of the corresponding flow rate.

$Q_3 = 10 \mu\text{l/min}$, the fuel concentration at the vicinity of the anode drops and the depletion boundary layer grows. For the flow rate of $Q_3 = 10 \mu\text{l/min}$, the concentration of formic acid over the anode ($y = -600 \mu\text{m}$) in the center of the electrode ($x = 2.5 \text{ cm}$) is almost zero. This fact reveals that just the first few millimeters of the electrode has significant contribution to current generation.

Sharp drop of fuel concentration over the anode at $y = -600 \mu\text{m}$ for $Q_3 = 10 \mu\text{l/min}$, Figure 4.10, is related to rapid fuel consumption over the electrode. This trend is observed for $Q_2 = 100 \mu\text{l/min}$, Figure 4.9, but because of faster replenishment of depletion boundary layer, the decline is not very sharp. The anode is made from carbon paper with thickness of $200 \mu\text{m}$, which occupies the channel height from $-800 \mu\text{m}$ to $-600 \mu\text{m}$. The catalyst layer is over the carbon paper at the channel height of $-600 \mu\text{m}$. The sharp drop of formic acid concentration from $-500 \mu\text{m}$ to the center of the channel at $x = 1 \text{ cm}$ is because of diffusion mixing of formic acid and electrolyte stream. The sharp decrease of formic acid concentration from $-500 \mu\text{m}$ to $-600 \mu\text{m}$ and from $-700 \mu\text{m}$ to $-600 \mu\text{m}$ is because of formic acid oxidation over the electrode and lack of fast replenishment of the depletion zone due to the low flow rate of formic acid.

At higher flow rates of 100 and $500 \mu\text{l/min}$, the fuel concentration over the anode is high enough to produce current, but only a part of the stream at the vicinity of the electrode is consumed. In this case, the core fuel stream with a high concentration just passes through the channel without contributing to current generation. Therefore fuel utilization at these two flow rates can be low.

An improved configuration can provide a larger active catalytic areas for electro-oxidation of fuel enhancing the fuel utilization as well as the fuel cell performance. Since the formic acid diffuses in to the electrolyte through the

Figure 4.8. Concentration profile of formic acid solution in the middle of the y-z plane for the fuel-to-electrolyte flow rate ratio of 1:1 and $Q_I=500 \mu\text{l/min}$.

liquid-liquid interface, the concentration of formic acid drops gradually over the anolyte stream.

Fuel concentration on the cathode is highly dependent on the flow rate of co-laminar flows. At $Q_I=500 \mu\text{l/min}$, the fuel concentration at the end of the cathode ($x = 4 \text{ cm}$) is almost zero, because the corresponding residence time of the flow in the channel of approximately 10 second is shorter than that of $Q_2=100 \mu\text{l/min}$ and $Q_3=10 \mu\text{l/min}$ (approx. 50 and 500 seconds).

In contrast, the corresponding values of fuel concentration of $Q_2=100 \mu\text{l/min}$ and $Q_3=10 \mu\text{l/min}$ are 120 and 260 mol/m^3 . This fuel crossover is significant at lower flow rates and has two consequences.

Figure 4.9 Concentration profile of formic acid solution at the middle of the y - z plane for the fuel-to-electrolyte flow rate ratio of 1:1 and $Q_e = 100 \mu\text{l/min}$.

Figure 4.10. Concentration profile of formic acid solution at the middle of the y - z plane for the fuel-to-electrolyte flow rate ratio of 1:1 and $Q_e = 10 \mu\text{l/min}$.

First, the concentration of fuel in the anolyte stream decreases leading to lower current density. Second, the electrooxidation of formic acid over the cathode can result in a mixed potential and decreases the open-circuit potential and the overall cell performance.

4.6.3 Concentration Distribution of Oxidant through the Fuel Cell

Microfluidic membraneless fuel cells with a stream of oxidant such as dissolved oxygen in sulfuric acid usually suffer from the low oxygen concentration over the cathode leading to low current density [60]. The strategy of using gas diffusion electrode as air-breathing cathode aims at providing higher oxygen content at the cathode [49]. In the numerical simulation, the cathode catalyst layer is considered as a boundary on the inner side of the channel where reduction of oxygen takes place, Figure 4.3. Also, oxygen can diffuse through the gas diffusion cathode into the aqueous streams in the channel. The simulated oxygen concentration through the gas diffusion electrode is shown in Figure 4.11.

Figure 4.12. to Figure 4.14 show a sharp drop of oxygen concentration in the electrolyte rather than in the electrode. This sharp drop is attributed to the

Figure 4.11 Concentration distribution of oxygen through the gas diffusion electrode and over in the channel at the maximum current density of the corresponding flow rate.

Figure 4.12 Concentration profile of oxygen at the middle of the y-z plane for the fuel-to-electrolyte flow rate ratio of 1:1 and $Q_I=500 \mu\text{l/min}$.

difference in the higher diffusion coefficient of oxygen in porous media ($D_{O_2(GDE)} = \varepsilon/\tau \times 2 \times 10^{-5} \text{ m}^2/\text{s}$) as compared to water ($D_{O_2(H_2O)} = 2 \times 10^{-9} \text{ m}^2/\text{s}$). The convective transport of co-laminar streams inside the channel also affects the transport of oxygen through the channel. At higher flow rates of $Q_I=500 \mu\text{l/min}$ and $Q_2=100 \mu\text{l/min}$, the transported oxygen cannot diffuse to the anolyte stream and washed away with the electrolyte stream. At the low flow rate of $Q_3=10 \mu\text{l/min}$, oxygen has more time to diffuse to the anolyte stream. The oxygen concentration over the catalyst layer at the end of the anode ($x = 4 \text{ cm}$) is around 35 mol/m^3 . For the case of Q_3 in Figure 4.14, there is a slight drop in the profile of oxygen concentration at $y=-600 \mu\text{m}$. The porous anode occupies the channel from $-600 \mu\text{m}$ to $-860 \mu\text{m}$ and the decrease is mainly related to the slower rate of oxygen diffusion in the porous anode ($D_{O_2(anode)} = 2.6 \times 10^{-10} \text{ m}^2/\text{s}$) as compared to a pure aqueous media.

Figure 4.13 Concentration profile of oxygen at the middle of the y - z plane for the fuel-to-electrolyte flow rate ratio of 1:1 and $Q_2=100 \mu\text{l/min}$.

Figure 4.14 Concentration profile of oxygen at the middle of the y - z plane for the fuel-to-electrolyte flow rate ratio of 1:1 and $Q_2=10 \mu\text{l/min}$.

4.6.4 Fuel Utilization and Power Density

Figure 4.15 shows the effect of increasing the flow rate from 10 to 500 $\mu\text{l}/\text{min}$ on fuel utilization at different flow rates. The improvement of power density at higher flow rates is associated with (i) the higher voltage generated due to the lower mixed potential at the cathode and (ii) the higher rate of electrochemical reaction to generate current due to the availability of reactants in the vicinity of the catalytic active sites. Current generation over the anode is highly dependent on the concentration of formic acid. Beside the low fuel concentration over the anode, the low open-circuit potential is another reason for the low power density of $Q_3=10 \mu\text{l}/\text{min}$.

The fuel utilization is defined as:

$$\varepsilon_{fuel} = \frac{J}{nFv_{fuel}} \quad (4.11)$$

where v_{fuel} represents the supply rate of the fuel in mol/sec. Figure 4.15 clearly shows that a higher fuel supply rate leads to a high power density but lower fuel utilization. At the flow rates of 10 $\mu\text{l}/\text{min}$, 100 $\mu\text{l}/\text{min}$ and 500 $\mu\text{l}/\text{min}$, the experimental fuel utilizations of the cell at maximum power density are 38.9%, 6.23% and 1.03%, respectively. At the same flow rates, the numerical fuel utilizations of the cell at the corresponding power densities are 49.6%, 7.21% and 1.95%, Figure 4.15. There is a good agreement between experimental and numerical results, but a quantitative difference is observed for the flow rate at 10 $\mu\text{l}/\text{min}$. Concentration loss can reduce the cell potential at high current densities and especially at low flow rates. Since the simulation does not include the impact of concentration losses on the cell potential, error in calculating the cell

Figure 4.15 Comparison of numerical and experimental fuel utilization at maximum power density.

potential could be introduced. Moreover, experimental uncertainties could be another source for this discrepancy.

As shown in Figure 4.7 to Figure 4.10, for the flow rates of 100 and 500 $\mu\text{l/min}$, the fuel concentration over the anode active area is high enough to produce more current, but only a part of the stream in the vicinity of the electrode is consumed. The core of the fuel stream with a high concentration just passes through the channel without any contribution to current generation. The high fuel utilization of the cell at 10 $\mu\text{l/min}$ is credited to the longer residence time in the channel.

As the flow rate of the streams decreases almost two orders of magnitude from 500 to 10 $\mu\text{l/min}$, the corresponding maximum power density only drops from approximately 7.9 to 3.9 mW/cm^2 . The fuel utilization increases from 1.03% to 38.9%.

The porous anode presents more active area than a non-porous and planar anode. The use of porous carbon paper in the channel serves the purpose of

Figure 4.16 Flow field simulation: (a) Simulated velocity field in the channel with the porous anode; (b) Velocity profile across the channel for the porous and non-porous anodes at a flow rate of 500 $\mu\text{l/min}$.

replenishing the depletion boundary layer. However, numerical simulation of the flow field with the porous anode reveals that the velocity of liquid in a porous medium is almost zero, Figure 4.16. Thus, there is no effective advective mass transport through the porous anode to provide fresh reactants to the active sites.

4.7 Conclusions

Advective mass transport across the channel from the middle of the fuel stream to the side walls, where reactive areas are located, does not occur effectively. Consequently, depletion boundary layer over the planar electrode cannot be replenished. The reactant concentration drops gradually along the anode. As the flow rate decreases, depletion boundary layer grows and only a part contributes to current generation. In addition, the fuel in the core of the fuel

stream passes through the channel without being used reducing fuel utilization. As a general design consideration, a compromise between high fuel utilization rate and high power density needs to be met. Hydrodynamic manipulation of the fuel stream can improve advective mass transport to replenish the depletion layer over the anode. The next chapter shows how flow architecture can improve the performance of air-breathing microfluidic fuel cells.

Chapter 5 Air-breathing Microfluidic Fuel Cell with Flow-Through Anode*

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Abstract

This chapter describes the detailed characterization of a laminar flow-based fuel cell (LFFC) with air-breathing cathode. The effects of flow-over and flow-through anode architectures, as well as operating conditions such as different fuel flow rates and concentrations on the fuel utilization and power density are investigated. Formic acid with concentrations of 0.5 M and 1 M in a 0.5 M and sulfuric acid solution as supporting electrolyte were used as fuel with varying flow rates of 20, 50, 100 and 200 $\mu\text{l}/\text{min}$. Because of the improved mass transport to the catalytic active sites, the flow-through anode showed improved maximum power density and fuel utilization per single pass as compared to a similar flow-over planar anode investigated in Chapter 4.

5.1 Introduction

In a microfluidic fuel cell, reactants are directed to a channel with reactive walls by a convective flow. The reactants subsequently diffuse to the catalytic sites on the walls. The steady-state diffusion-limited mass transport to a reactive site in a pressure-driven flow is known as the Graetz problem and is usually divided into two main regimes: the *entrance regime* and the *fully developed regime* [97]. Graetz number ($Gz = zh^{-1}Pe^{-1}$) represents the ratio between the convective time scale ($\bar{t}_c = zU^{-1}$) and the diffusive time scale ($\bar{t}_d = h^2D^{-1}$) [97], where z is the axial position along the channel and h is the channel height which represents the characteristic length scale. $Pe = (UhD^{-1})$ is the Peclet number and U is the axial flow velocity in the channel [97].

For a microfluidic fuel cell with flow-over electrodes, consumption of fuel and oxidant forms depletion layers with low reactant concentration over the electrodes. As reactant flow rate increases, diffusion time scale becomes much greater than the axial convective time scale, resulting in a diffusion-limited performance ($Gz \ll 1$), Figure 5.1. Therefore, a thin depletion boundary layer (δ) over the electrode ($\delta \ll h$) is formed and a mass transfer *entrance regime* appears [97]. Running on a high flow rate of reactant, high power density is achieved from the cell, but because of the rapid convective mass transport to the cell exit, a portion of the reactant does not reach the reactive sites. The low reactant consumption makes the performance becomes diffusion dominated. As reactant utilization increases, a bulk depletion of reactants takes place through the channel, and a mass transfer in *fully developed regime* arises. In this regime, reactant consumption is high indicating high fuel/oxidant utilization. But the power density drops as compared to the operation in higher flow rates, Figure 5.1. Transition

from *entrance regime* at high flow rates to *fully developed regime* at low flow rates reveals a trade-off between power density and fuel utilization, which has been reported frequently [30, 43, 63, 98].

To understand the relationship between fuel utilization and power density, interaction between mass transport and electrochemical reactions should be considered as well. The Damköhler number is defined as the ratio between the time taken by the mass transport and the time taken by the reaction over the reactive sites [97]. For the purely diffusive mass transport, the Damköhler number is defined as $Da = kC^{X-1}hD^{-1}$, where k , C , X and D are the rate constant, concentration, order of reaction and diffusivity.

To evaluate the effect of flow architecture on the cell performance, Kjeang and co-workers selected three fuel cell designs running on all vanadium redox solutions as fuel and oxidant [24]. The vanadium redox fuel and oxidant provide a well-balanced electrochemical half cells for reaction rates and transport kinetics with no catalyst [24]. The three designs have different electrode structures and flow architectures. The one with planar flow-over graphite rod electrodes has a diffusion length of 150 μm [30], while the other one has flow-over porous electrodes with a diffusion length of 120 μm [80]. For the design with flow-through porous electrodes [48], diffusion length of 36 μm was assumed which is the average fiber spacing of the porous carbon paper-based electrodes [80].

Diffusion length scale to reactive sites should be decreased to improve reactant utilization. Decreasing the channel height or using porous electrodes decrease the diffusion length scale. As shown in Figure 5.1, decreasing the diffusion length scale increases the maximum power density and fuel utilization per single pass at a given flow rate. Improvement in terms of power density and

Figure 5.1 Gz - Da plot for representative microfluidic fuel cells. Fuel and oxidant are 2 M vanadium redox species (V^{2+}/V^{3+} , VO_2^+/VO^{2+}) in 2 M sulfuric acid as supporting electrolyte. No catalyst was used. Values in the parentheses refer to maximum power density, fuel utilization at cell potential of 0.8 V and flow rate (mW/cm², %, μl/min). (■) flow-over planar graphite electrodes; (●) exploited flow-over porous carbon paper while (▲) refers to flow-through porous carbon paper electrodes. To calculate Da number for fuel stream, constant rate (k) and diffusivity (D) for V^{2+}/V^{3+} were assumed to be 1.7×10^{-7} m/s and 2.4×10^{-11} m²/s, respectively [85].

fuel utilization is achieved for the design with flow-through porous electrodes.

This performance improvement is an indication of enhanced mass transport through the *extended reactive sites* of the porous electrodes with continuous replenishment of depleted reactants.

In this chapter, the diffusion length scale at the anode is reduced by implementing a *flow-through* anode in an air-breathing LFFC. This design provides a platform to explore the impact of anodic flow architecture on the overall performance and the fuel utilization per single pass. Similar to the work of Yoon et al. [42], the present flow-through anode has infinite fuel entry points in a simple design. An air-breathing LFFC with a *planar flow-over* anode was also fabricated with the same dimensions and using the same materials to create a benchmark platform for performance evaluation.

Carbon dioxide is a product of formic acid or methanol electrooxidation. At high current densities, carbon dioxide bubbles may appear in the channel. Bubble dynamics influences local species transport, liquid-liquid mixing and crossover [32]. The effect of bubbles on cell performance becomes significant as the flow rate decreases. While the investigations available in the literature usually exploited fuel rates of 300 $\mu\text{l}/\text{min}$ and higher [49, 54, 55] for characterization, the present investigation attempted to characterize the performance and fuel utilization per single pass at medium to low flow rates of less than 200 $\mu\text{l}/\text{min}$. In addition, to investigate the role of fuel concentration on cell operation at low flow rates, potential sweep voltammetry and chronoamperometry experiments were run on two fuel solutions of 0.5 M and 1 M formic acid with 0.5 M sulfuric acid as supporting electrolyte.

5.2 Fabrication and Characterization

Electrode fabrication and cell characterization were described in detail in Chapter 3. Both planar and flow-through designs were fabricated from the same materials with the same geometrical dimensions unless stated otherwise. Anode and cathode of both planar and flow-through designs have the same reactive area of $3 \times 30 \text{ mm}^2$.

A groove with the same size of the anode and depth of 0.4 mm is machined into the graphite plate by a desktop 3D milling machine (Roland[®] DG Corporation, model MDX-40A) to accommodate the anode and works as a current collector, Figure 5.2. To enable the fuel to pass through the anode, a slit was machined through the graphite current collector, Figure 5.3.

The main flow channel was made of poly(methyl methacrylate) (PMMA) (Margacipta[®]) with a thickness of 1.5 mm. PMMA is resistant to sulfuric acid and

Figure 5.2. Schematic of the fabricated fuel cell architecture with planar flow-over anode; (a) exploded view; (b) cross-sectional view, not to scale.

formic acid at room temperatures. The volume of the channel in both designs is 135 microliters. The depth of the channel is determined by the thickness of the PMMA plate. Since half of the channel is filled with fuel, the amount of fuel in the channel is about $65\text{ }\mu\text{l}$ while another half of the channel is filled only with supporting electrolyte. Double-sided adhesive was used to attach the channel to the graphite plate which accommodates the anode.

The main objective of this investigation is the relationship between the flow architecture and the fuel cell performance. In order to make a direct comparison, two fuel cells were fabricated from the same materials to have similar initial OCVs and Ohmic resistance.

To evaluate the combined Ohmic cell resistance, electrochemical impedance spectroscopy (EIS) was carried out at the open-circuit potential (OCV) and a flow rate of 200 $\mu\text{l}/\text{min}$. Frequency of EIS ranges from 0.1 Hz to 500 kHz with an AC amplitude of 10 mV rms. The intercept of high-frequency impedance spectrum with real axis indicates the total cell resistance of $2.03 \pm 0.33 \, \Omega$ and $1.83 \pm 0.32 \, \Omega$ for planar and flow-through designs, respectively. These values reveal that both fuel cell designs have almost the same Ohmic losses. Figure 5.4 depicts the assembled cell.

Figure 5.3. Schematic of the fabricated fuel cell architecture with planar flow-through anode; (a) Cross-sectional view; (b) Exploded view, not to scale.

Figure 5.4. A view of the fabricated fuel cell with flow-over anode. Fuel inlet is on the other side of the cell, not shown in this view.

5.3 Results and Discussions

To find the optimum range of flow rate that produces a maximum power density, linear sweep voltammetry for both designs was carried out and the corresponding power densities were plotted. As shown in Figure 5.5, the maximum power density has only an increase of 10% and 7% for planar and flow-through design as the flow rate increases from 200 $\mu\text{l}/\text{min}$ to 400 $\mu\text{l}/\text{min}$. For flow rates lower than 200 $\mu\text{l}/\text{min}$, the maximum power density reduces dramatically as the flow rate decreases. Therefore, flow rates of 200 $\mu\text{l}/\text{min}$, 100 $\mu\text{l}/\text{min}$, 50 $\mu\text{l}/\text{min}$, 20 $\mu\text{l}/\text{min}$ with corresponding Reynolds number of 2.96, 1.48, 0.74 and 0.296 were selected to investigate the effect of anode flow architecture on fuel cell performance.

As a comparison, the present maximum power density of 19 mW/cm^2 is lower than the maximum power density of 26 mW/cm^2 of an air-breathing design with planar anode at 300 $\mu\text{l}/\text{min}$ [49]. But at a lower flow rate of 100 $\mu\text{l}/\text{min}$, the present maximum power density of 18 mW/cm^2 is much higher than 10 mW/cm^2 from [49]. The previous cell had a channel height of 2 mm, an anode length of 20.5 mm and a total active area of 0.62 cm^2 with 10 mg/cm^2 of Pd catalyst

Figure 5.5 Maximum power density vs. running flow rate for planar and flow-through (FT) design with 1 M formic acid.

particles on graphite plate. These differences can be attributed to the usage of catalyst-covered carbon paper as anode and the channel dimensions in the present study.

5.3.1 Fuel Cell Performance Running on 1 M Formic Acid

The typical current-potential and current-power curves at different flow rates for planar and flow-through designs are shown in Figures 5.6 and 5.7. Three distinctive regions with the dominant losses of activation, Ohmic and mass-transport are obvious for both designs. As the flow rate decreases, the OCV drops mainly because of the widening inter-diffusion region and the resulting mixed potential over the cathode. Generally, flow-through design exhibits a higher performance as compared to the planar design. For instance, at a flow rate of 200 μl/min, or a Peclet number of 880, flow-over design has respective maximum

power density and current density of 19.4 mW/cm^2 and 90 mA/cm^2 , while the flow-through design has the corresponding values of 26.5 mW/cm^2 and 120 mA/cm^2 . The maximum power density of the planar design for flow rates of 200, 100, 50 and $20 \text{ }\mu\text{l/min}$ are 19.4 ± 4.34 , 17.9 ± 5.34 , 14 ± 3.34 and $9.87 \pm 3.54 \text{ mW/cm}^2$ compared to 26.5 ± 4.20 , 19.8 ± 4.20 , 13.4 ± 1.81 and $11.4 \pm 1.20 \text{ mW/cm}^2$ of the flow-through design. Along with the data shown in Figure 5.5, these results provide an evidence for the improvement of mass transport in fuel cell with flow-through anode.

Figure 5.6 Performance of planar design running on 1 M formic acid: (a) potential versus current density and (b) Power density versus current density.

Higher power densities of flow-through design are mainly credited to the quick replenishment of used reactants. In addition, flow-through architecture allows the improved utilization of the reactive sites inside the porous electrode. Since the fuel is supplied from the bottom, a relatively constant concentration of fuel over the anode can be provided. The flow-over anode was made of porous carbon paper, but numerical simulation showed that the full depth of the anode does not contribute to current generation because of the lack of advective mass transport. As observed in Chapter 4, growth of depletion boundary layer on a flow-over anode only benefits the first few millimeters of the electrode.

For both designs, mass-transport losses became significant at potentials lower than 0.4 V for all flow rates, except the high flow rate of 200 $\mu\text{l}/\text{min}$. Accumulation of reaction products, such as carbon dioxide and slow replenishment of depletion boundary layer can be the major reasons for mass-transport losses.

The buildup of carbon dioxide over the anode may results in bubble generation. Carbon dioxide bubbles generated in the channel create two main problems [78]. First, they can fill the channel and change the interface of the two streams, or even mix up the two streams completely, resulting in a crossover phenomenon. Mixing of fuel with electrolyte stream causes parasitic current and decreases the overall cell current [99]. Second, bubbles block the active sites for fuel oxidation and the effective area of anode reduces. Periodic growth and detachment of bubbles within the channel leads to discontinuous flow field along the channel causing an unstable fuel cell operation, as some anomalies can be observed in Figure 5.7.

Figure 5.7 Performance of flow-through design running on 1 M formic acid: (a) Potential versus current density; and (b) Power density versus current density.

5.3.2 Fuel Cell Performance Running on 0.5 M Formic Acid

In order to investigate the effect of fuel concentration on the cell performance, 0.5 M formic acid was used as fuel. As shown in Figure 5.8 and Figure 5.9, the OCV of both designs at lower flow rates of 20 and 50 $\mu\text{l}/\text{min}$ are slightly higher than that of 1 M formic acid because of the lower fuel concentration gradient from anode to cathode.

In agreement with the results using 1 M formic acid, the maximum power density of the planar design is lower than that of the flow-through design. Maximum power densities at flow rates of 200, 100, 50 and 20 $\mu\text{l}/\text{min}$ are 17.8 ± 1.38 , 17.5 ± 1.34 , 16.1 ± 1.73 and 7.70 ± 0.52 mW/cm^2 , respectively, while the flow-through design has the corresponding power densities of 20.5 ± 2.06 , 18.4 ± 0.68 , 16.7 ± 0.51 and 10.4 ± 1 mW/cm^2 .

The sharp drop of cell potential for the flow-over design running at low flow rates of 20 and 50 $\mu\text{l}/\text{min}$, Figure 5.8, compared to the cell potential of the flow-through design running at the same flow rates, Figure 5.9, is highly associated with the slow local transport of species to active sites and the sluggish removal of carbon dioxide from catalytic areas. In contrast, the flow-through design shows a better polarization behavior. In the very low flow rate regime, the fuel cell performance is dominated by diffusive transport from the bulk [80].

Running the cell on 50 $\mu\text{l}/\text{min}$ of formic acid shows a Coulombic fuel utilization of $43 \pm 3\%$ per single pass as calculated by Equation (4.11) at the point of maximum power density for both planar and flow-through designs.

Figure 5.8 Performance of flow-over design running on 0.5 M formic acid: (a) Potential versus current density; (b) Power density versus current density.

The sharp drop at 20 $\mu\text{l}/\text{min}$, Figure 5.8, is basically associated with very low flow rate with planar flow-over anode. At low flow rate of 20 $\mu\text{l}/\text{min}$ of formic acid with 0.5 M concentration, fuel can be depleted very fast over the electrode. In addition, accumulation of by-products from formic acid oxidation can hinder fuel transport to active sites of the anode. Consequently, a sharp drop in cell current is observed. The slight retrieval of cell current at potentials lower than 0.2 V can be related to removal of CO_2 bubble(s) from the cell channel by stream drag force which more anode active sites are able to have contribution in current generation. For the same flow rate with flow-through anode, Figure 5.9, the continuous replenishment of the anode from bottom can facilitate the mass transport to active sites and avoid a sharp drop in current generation.

Figure 5.10(a) shows that the current at cell potential of 0.4 V decreases as the flow rate decreases. At each flow rate, four different tests show a similar trend.

However, experimental results using 1 M formic acid shows a slight improvement compared to 0.5 M formic acid. For the planar design at 200 $\mu\text{l}/\text{min}$ of 1 M formic acid, the average current and the associated fuel utilization are 41.4 ± 5.63 mA and $6.31 \pm 1.1\%$. For the same design and 50 $\mu\text{l}/\text{min}$ of 1 M formic acid, the current and fuel utilization are 32.0 ± 4.9 mA and $49.9 \pm 8.2\%$, Figure 5.10(b). In this case, the amount of fuel introduced into the channel decreases by 400%, but the current only shows a drop of 22%. Two conclusions may be drawn here. First, the number of available sites for electrooxidation is far lower than required. Second, the residence time of the fuel at the vicinity of catalytic active area may play a critical role [100]. As the flow rate decreases to 50 $\mu\text{l}/\text{min}$, the fuel residence time in the channel increases four times and may increase the probability of more successful interactions between fuel and the active sites.

Figure 5.9 Performance of flow-through design running on 0.5 M formic acid: (a) Potential versus current density; (b) Power density versus current density.

Figure 5.10 Performance comparisons of the two designs running on 0.5 M and 1 M formic acid in terms of (a) current density at 0.4 V cell potential and (b) fuel utilization at 0.4 V cell potential as a function of the flow rate.

5.4 Long-term Performance

The scanning process of potential sweep voltammetry from OCV to zero potential took up to 3 minutes for each experiment. The cell experienced a transient mode of operation during the measurement. Therefore, potential sweep voltammetry represents a complex and time-dependent function of a large number of coupled physical and chemical parameters. In this case, the discrimination of the effect of an individual phenomenon on the cell performance becomes very difficult, and in some cases even impossible.

To distinguish the effect of flow architecture on the cell performance, a long term performance test (chronoamperometry experiment) was carried out at the flow rate of 100 $\mu\text{l}/\text{min}$. Since the cell potential is fixed during a long term operation, effect of flow architecture, flow rate and fuel concentration can be observed more clearly.

To limit the degradation of performance due to carbon monoxide poisoning, fresh cells were used for long term performance at a cell voltage of 0.4 V and the maximum power density. A rapid degradation in current generation was observed, probably because of the formation of carbon monoxide (CO) as an intermediate species, which can occupy the active sites.

Further experiments were carried out at a cell potential of 0.2 V to capture the effect of flow architecture on the long-term performance of the fuel cell. At this cell potential, the anode has a higher overpotential which facilitates the oxidation of carbon monoxide. Therefore a more stable performance was observed.

As shown in Figure 5.11, operating at two fuel concentrations of 0.5 M and 1 M, flow-through design has a higher average current density of $34.2 \pm 2.69 \text{ mA}/\text{cm}^2$ and $52.3 \pm 14.1 \text{ mA}/\text{cm}^2$ and an average fuel utilization of

16.3±4.6% and 21.4±1.68% as compared to the planar design with corresponding values of 25.1±1.11 mA/cm² and 35.5±2.2 mA/cm² and fuel utilization of 11.1±0.7% and 15.7±0.7%.

Because of the enhanced mass-transport characteristics at the anode side, overall cell current density with flow-through anode running on 0.5 M formic acid at 0.2 V (34.2 mA/cm²) is almost the same as that of the cell with flow over a planar anode (35.47 mA/cm²) running on 1 M formic acid at a fuel flow rate of 100 µl/min.

The improved cell current indicates that flow-through anode can exploit more fuel for electrooxidation reaction. Since fuel is introduced to the channel through the electrode, the depletion boundary layer is replenished effectively. In contrast to the planar design, more fuel molecules have the chance to come into contact with the catalytic active area. In a planar design, the fuel volume in the middle of the channel just passes through without interacting with the catalyst layer.

For all four sets of experiments, a gradual current degradation was observed. The degradation is associated with CO poisoning of the anode catalyst and accumulation of CO₂ on the catalytic active sites. The fluctuations may be related to intermittent feeding of fresh reactant to the active sites because of the formation of CO₂ bubbles as a product of formic acid electrooxidation.

The solubility of CO₂ in water at room temperature is 178 mg/100 ml, which is equivalent to 0.0404 M. If carbon dioxide and protons are assumed to be the only products of the electro oxidation of formic acid, the concentration of the produced carbon dioxide during one minute operation of cell with planar anode running on 100 µl/min of 1 M formic acid and 0.5 M electrolyte and a total flow rate of 200 µl/min (with the average current density of 34.2 mA/cm²) is estimated

as 9.8×10^{-6} M. At this flow rate, the saturation threshold of CO_2 dissolution in the channel is 8.1×10^{-6} M which is almost the same as the concentration of the produced carbon dioxide. As a result, the fluctuations in current are not significant. If the amount of CO_2 generated in the channel is beyond the saturation threshold, bubbles start to form in the channel. Therefore, the fluctuations shown in Figure 5.11(a) can be associated to the emerging bubbles in the channel.

As observed in Figure 5.6 to Figure 5.9, fluctuations of current densities higher than 40 mA/cm^2 were observed. The main cause for this behavior is the formation of CO_2 bubbles. Since flow-through design has a higher fuel utilization rate, the chance of bubble generation is higher. At high flow rates, bubbles formed in the channel could detach from the anode and be washed away towards the outlet. However, at a moderate flow rate, bubbles remain attached to the channel walls. Bubbles can block the anode active sites and reduce the current density. Therefore, the partial channel block may change the range of the average current density from experiment to experiment as reflected in the error band of the average current density for flow-through design running on 1 M formic acid.

Figure 5.11 Long term performance comparison of two designs of flow-over (planar) and flow-through (FT) running on 0.5 and 1 M formic acid and flow rate of $100 \mu\text{l}/\text{min}$; (a) Chronoamperometry experiment at cell potential of 0.2 V; (b) Average current density and fuel utilization from the chronoamperometry experiment for two designs.

5.5 Conclusions

This chapter discusses the performance of two air-breathing laminar flow-based fuel cells running on formic acid with flow-over and flow-through anode architectures. Medium to low flow rates of fuel and electrolyte were utilized to explore the impact of the flow architecture on the performance. Improved maximum current density and fuel utilization in LFFC with flow-through anode demonstrated the enhanced mass-transport at the anode side. This approach can utilize a higher fraction of the fuel introduced to the channel as compared to the flow-over anode. However, the flow-through design experiences a higher pressure drop. For practical applications, an air-breathing fuel cell should be able to operate at medium to low flow rates with high power density and fuel utilization. In the case of using formic acid and methanol, the formation of CO_2 bubbles at high current densities plays an important role on the cell performance. On the one hand, cell operation at low flow rates and high power density is a requirement. On the other hand, removal of reaction products and bubbles from the active sites, which can decrease the overall performance, is a challenging problem at low flow rates. Consequently, a trade-off between power density and flow rate exists for the current designs of air-breathing LFFCs. Breaking this trade-off needs a revolutionary design to enable a cell operates at a low flow rate with high performance.

For practical long-term operations, fuel cells should have high efficiency and power by running at higher potentials, e.g. 0.4 V. Durability and performance of the anode can be improved by incorporating appropriate catalysts.

The next chapter provides a novel solution for addressing the problem of the bubble formation, opening a new direction for possible practical applications of LLFCs.

Chapter 6 An Air-breathing Microfluidic Fuel Cell with Fuel Reservoir*

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Abstract

This chapter describes the design and characterization of an air-breathing microfluidic fuel cell with a stationary fuel reservoir above the anode replacing the conventional continuous fuel stream. Unlike other air-breathing microfluidic designs, the fuel is not in direct contact with electrolyte stream allowing the use of high fuel concentration. In addition, Ohmic losses are minimal because of the low anode-to-cathode spacing. Since the fuel passes through the catalyst layer over the anode, depletion boundary layer does not form. Improved mass transport compared to previous microfluidic designs is obtained because of the uniform fuel concentration over the anode and efficient bubble removal from the anode active sites.

6.1 Introduction

As observed in Chapter 5, fuel utilization increased in a fuel cell with flow-through anode. But the chance of carbon dioxide bubble formation in the flow channel also increases the hindering of fuel transport to the active sites and the disturbing of the fuel-electrolyte interface. In addition, bubble formation in the channel increases the total Ohmic loss because of the reduced area available for charge transport between the electrodes. An air-breathing microfluidic fuel cell should be able to operate at medium to low flow rates with a high power density and high fuel utilization. In the case of using formic acid or methanol, removal of reaction products and bubbles from the active sites becomes difficult at lower flow rates. In addition, utilization of fuel with high concentration degrades the cell performance dramatically because of the large interface between the fuel and the electrolyte stream and the subsequent diffusive mixing and fuel crossover in the current designs [49]. Breaking this trade-off requires a different fuel delivery solution for air-breathing microfluidic fuel cell.

6.2 Fuel Cell Fabrication

A design of air-breathing microfluidic fuel cell with fuel reservoir above the anode and a stream of electrolyte is proposed to address the issues of fuel delivery and bubble formation, Figure 6.1. A uniform fuel concentration is supplied over the reactive sites of the anode and the bubbles can be released freely to the fuel reservoir.

The anode of the fuel cell was made of plain Toray carbon-fiber-based paper with a typical thickness of 280 μm and a porosity of approximately 78%. This carbon paper was originally used as gas-diffusion-electrode for proton exchange

membrane fuel cells (PEM fuel cells). The anode contains a catalyst layer made of palladium black (Pd) with a loading of $7\text{--}8\text{ mg cm}^{-2}$ [101]. To make the catalyst ink, high-surface-area Pd black particles (99.9% metal basis) from Alfa-Aesar were mixed with carbon nanoparticles (Vulcan X72) with a loading of 1 mg cm^{-2} . Nafion solution with a loading of 3 mg cm^{-2} was used as the binder. Isopropanol was added to the mixture followed by ultrasound sonication for 1 hour to obtain a low viscosity of the ink. The resulting catalyst ink was spread over a piece of carbon paper with a size of $10\times 10\text{ cm}^2$ manually and dried under a fume hood for 20 minutes and subsequently kept in an oven at a temperature of $80\text{ }^{\circ}\text{C}$ for 1 hour. The cathode was made of carbon-fiber-based paper as used in Chapter 5 [101]. The cathode was purchased from Alfa Aesar (stock No. 45375) which is originally designed to be used as a cathode for direct methanol fuel cells.

The microfluidic fuel cell consists of a 0.5 mm-thick silicon-rubber layer to form the flow channel. Similar to the designs reported in Chapter 5, the fluidic channel has a length and width of 30 mm and 3 mm, respectively. The channel depth is determined by the thickness of the silicon rubber, which was cut using a CO_2 laser machining system (Universal M-300 Laser Platform, Universal Laser Systems Inc.). Since the channel is made in flexible silicon rubber, the device is self-sealing.

Figure 6.1 Air-breathing microfluidic fuel cell with fuel reservoir: (a) The exploded view; (b) The assembled cell and the operation of the air-breathing microfluidic fuel cell with a pressurized fuel reservoir. Electrolyte stream is introduced into the channel through an inlet.

Figure 6.2 A view of the fabricated fuel cell with fuel reservoir on top the anode.

As shown in Figure 6.1, in order to accommodate the electrodes in the current collectors, a slit was machined into the same graphite plates using a desktop three-dimensional milling machine (Roland[®] DG Corporation, model MDX-40A). Electrode strips were fixed on the edges of the slit using a conductive epoxy containing silver particles (CircuitWorks[®] Conductive Epoxy from Chemtronics[®]). Both electrodes were aligned with the channel to maintain 0.9 cm^2 anodic and cathodic catalytically-active surface area. The flow channel was sandwiched between two graphite current collectors. Fluidic interconnects for handling the streams were glued to the graphite plates using a fast drying epoxy. The fabricated cell was inspected for leakage using DI water from Millipore system. The assembled cell is shown in Figure 6.2.

6.3 Characterization

The fuel cell characterization tests were carried out using fuel containing formic acid with 1 M and 3 M concentrations including 0.5 M sulfuric acid as a supporting electrolyte and 0.5 M sulfuric acid as the electrolyte stream. For all experiments discussed in earlier chapters, 1 M formic acid was used as a baseline

Figure 6.3 Open-circuit potential versus time after filling the fuel reservoir and applying pressure of 3 mbar. Fuel concentration is 3 M.

concentration. In addition, it was discussed that using high fuel concentration does not improve the overall cell performance because of low fuel utilization at single pass for the cells with flow-over and flow-through anodes. In order to investigate the influence of fuel concentration on the overall performance of this new design of fuel cell, 3 M formic acid was used for the characterization experiments.

The flow rate of the electrolyte stream was kept constant for all experiments. Electrolyte stream was delivered by a syringe pump (KD Scientific). Fuel was supplied from the chamber above the anode, where it was directly exposed to the anodic catalyst layer. The performance of the fuel cell was characterized under atmospheric condition and under a gauge pressure of 3 mbar.

For all experiments running under the condition of gauge pressure, electrolyte was first introduced into the flow channel using a syringe pump to avoid fuel crossover to the cathode side. Then, the chamber was filled with the fuel and

connected to a pressure regulator (PPC4-ui, Fluke, USA). Figure 6.3 shows the changes of open-circuit potential after filling the fuel reservoir. For all experiments, the open-circuit potential (OCV) was monitored until it reaches a stable value. Figure 6.4 shows the EIS curve of the cell at open-circuit potential. This design has an average Ohmic resistance of $0.6\ \Omega$ which is lower than the resistance of the cells discussed in Chapter 5.

Figure 6.4. Impedance spectra obtained at open-circuit potential.

6.4 Results and Discussions

Figure 6.5 compares the performance of the fuel cell under the two conditions. At atmospheric pressure, mass transport overpotential dominates the performance. A current density of $50\ \text{mA}/\text{cm}^2$ and a maximum power density of $14\ \text{mW}/\text{cm}^2$ were obtained. The behavior is characteristic for a mass transport-limited operation, because of the pure diffusive mass transport to the reactive sites. At a gauge pressure of 3 mbar, a limiting current density of $140\ \text{mA}/\text{cm}^2$ and a maximum power density of $29\ \text{mW}/\text{cm}^2$ were achieved. Higher maximum power density is an indication of improved mass transport to the active sites due to the convective mass transport. The open-circuit potential of the cell running under

Figure 6.5 Polarization curves for the air-breathing microfluidic fuel cell with atmospheric and pressurized fuel reservoir at a gauge pressure of 3 mbar, both running on 3 M formic acid at room temperature of 25°C. Scanning rate was 5 mV/sec. (■) and (□) refer to current-potential curve and current-power curve at no pressure applied, while (●) and (○) refer to current-potential curve and current-power curve at a pressure of 0.32 kPa applied to fuel reservoir.

gauge pressure was observed to drop slightly. This effect is associated with the fuel crossover to the cathode side.

To investigate the effect of fuel concentration on the cell performance, 1 M and 3 M formic acid were used. The gauge pressure of the fuel reservoir was kept constant at 3 mbar for both concentrations. A maximum power density of 18 mW/cm² was obtained using 1 M formic acid which is quite comparable to the maximum power density of 20 mW/cm² from of the flow-through design running at 100 µl/min as described in Chapter 5.

Figure 6.6 clearly shows that the increment of fuel concentration from 1 M to 3 M can improve the current density from 18 mW/cm² to 29 mW/cm². For conventional air-breathing microfluidic fuel cells with co-laminar interface in the

Figure 6.6 Polarization curves for an air-breathing microfluidic fuel cell with pressurized fuel reservoir, running on 1 M and 3 M formic acid at room temperature of 25°C and an applied pressure of 3 mbar. Scanning rate was 5 mV/sec. (■) and (□) refer to current-potential curve and current-power curve using 1 M HCOOH, while (●) and (○) refer to current-potential curve and current-power curve using 3 M HCOOH in the fuel reservoir.

middle of the channel, a high fuel concentration increases the diffusive fuel crossover and decreases the performance [49]. In this design with the fuel reservoir, fuel-electrolyte interface is restricted and a high fuel concentration can be used. Unlike the flow-over planar anodes, depletion boundary layer is not formed on the reactive sites in this flow architecture and a uniform fuel concentration is provided over the anode. Pressure of the fuel reservoir can be optimized according to the fuel concentration to overcome mass transport limitations and to improve fuel utilization. The obtained maximum power density of 18 mW/cm² is comparable to the maximum power density of 20 mW/cm² from the previous flow-through design of Chapter 5 at 100 μ l/min.

To observe the long-term performance of the air-breathing microfluidic fuel cell, a chronoamperometry test was conducted for cells running on 1 M and 3 M

Figure 6.7. Chronoamperometry test for an air-breathing microfluidic cell with fuel reservoir containing 1 M and 3 M formic acid. Pressure of reservoir with 1 M fuel was 3.3 mbar while the pressure of the reservoir with 3 M was 3 mbar.

formic acid, Figure 6.7. For the case of 1 M, the reservoir containing 0.8 ml formic acid was pressurized slightly higher than in the case of 3 M fuel to avoid mass-transport limited operation. An average current density of 68.8 mA/cm^2 and a corresponding fuel utilization of 22% were achieved over a time period of 8 minutes. The corresponding estimated fuel flow rate was $95 \mu\text{l/min}$. This performance has improved compared to the air-breathing cell with flow-through anode running on $100 \mu\text{l/min}$ of 1 M formic acid whose fuel utilization and average current density are 16.3% and 52.3 mA/cm^2 , respectively.

In addition, using 1 ml of 3 M fuel, the cell produced an average current density of 86 mA/cm^2 and a fuel utilization of 9% over a time span of ten minutes. As shown in Table 6.1, the improved fuel utilization and current density compared to the designs with flow-over and flow through anodes, reported in Chapter 5 were

Table 6.1. Performance comparison of different designs of air-breathing microfluidic fuel cells studied in this these. Fuel is a 1 M formic acid. Flow rate for flow-over and flow-through anodes is 100 $\mu\text{l}/\text{min}$. while flow rate for fuel reservoir on top of anode is 96 $\mu\text{l}/\text{min}$.

	Flow-over anode	Flow-through anode	Fuel reservoir on top of anode
Average current density (mA/cm ²) from long term test at cell voltage of 0.2 V	35	52	68
Fuel Utilization (%) from long term test at cell voltage of 0.2 V	11	16	22

mainly credited to the enhanced mass transport through the anode. Since the catalyst layer is located on top of the electrode, CO₂ bubbles were produced in the reservoir and released into the fuel chamber. Consequently, bubble formation in the channel is no longer a major issue. Furthermore, a continuous fuel supply is provided over the anode and the issue of low fuel replenishment does not exist. In conventional designs of air-breathing microfluidic fuel cells with flow-over anodes, fuel flow rate should increase to overcome the slow mass transport to the depleted regions over the anode. As a result, the fuel utilization per single pass drops.

The large fluctuations in current density of 3 M operation over 100 second could be caused by bubble formation in the channel and the subsequent release through the outlet. Since the catalyst layer was spread over the carbon paper, there is a chance for catalyst particles to penetrate through the electrode and reach the other side. Consequently, formic acid could be oxidized over the electrode exposed to the flow channel and bubbles could form. A bubble can block the channel for a short period until it is washed to the channel outlet by the drag force of the electrolyte stream.

6.5 Conclusions

In this chapter, the issue of bubble removal from the flow channel of an air-breathing microfluidic fuel cell was addressed. Bubbles from formic acid electrooxidation were released into the fuel chamber. Unlike the flow-over anodes, depletion boundary layer over the anode was not formed and a uniform fuel concentration was supplied. Since fuel was introduced to the anode through the top side wall of the channel, the channel depth was reduced and the whole design could be further miniaturized leading to a lower Ohmic resistance as compared to the designs with flow-over anodes.

It is worth mentioning that fuel density increases as its concentration becomes higher. In a vertically-layered liquid-liquid interface, where the dense stream is on top of the another stream with lower density, faster mixing between the two streams may occur [90]. In the current flow architecture, after the introduction to the channel through the porous anode the fuel is stacked over the electrolyte stream. The chance of fuel crossover to the cathode side can be enhanced. For further developments, as a substitute for the high electrolyte flow, a thin layer of Nafion can be coated over the cathode to decrease the cross-sectional area between the fuel and the active sites of the cathode as reported in [55].

Through optimizing the anode catalyst and the pressure of the fuel reservoir, higher fuel utilization per single pass can be achieved. Carbon paper-based anode can be treated to become hydrophobic to increase the applied pressure to the fuel chamber and to avoid the probable leakage from the electrolyte stream to the fuel channel.

The design allows the use of a fuel cartridge for passive delivery. An ideal stacking scheme is to connect several anodes to a single fuel reservoir containing

highly concentrated fuel through a microfluidic network. But to achieve this goal, some modifications for bubble handling from anodes side should be considered.

Results from Chapter 4 to Chapter 6 reveal that fuel cell overall performance can be improved greatly by hydrodynamic manipulation of the reactants streams. All conventional microfluidic fuel cells need to have three reservoirs for fuel, oxidant, or electrolyte in case of using air-breathing cathode, and waste products to provide continuous flows of reactants. In addition, controlling fuel cross over and diffusive mixing needs careful attention of managing reactant streams through the channel. From fluidic handling point of view, such design constraints hinder the integration of the fuel cell system with a power consumer in practical applications. Addressing this issue may need a totally different approach in designing a membraneless fuel cell. In the next chapter, a fuel cell is realized in a single compartment where the whole system can run on one reactant as both fuel and oxidant.

Chapter 7 Membraneless Hydrogen Peroxide Fuel Cell with Selective Electrodes*

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Abstract

This chapter reports the proof-of-concept for a high performance membraneless micro fuel cell running on hydrogen peroxide as both fuel and oxidant in a single chamber. The key concept is based on selective electrodes for separated oxidation and reduction mechanisms.

7.1 Introduction

The previous chapters show that fuel flow rate of an air-breathing microfluidic fuel cell should decrease to an optimal value to achieve a higher fuel utilization per single pass. Because of diffusive mixing of fuel with electrolyte, the flow rate should be kept above a threshold. Fluidic management of fuel and electrolyte (or oxidant) streams add complexity to the system design. Such design constraints prohibit the implementation of microfluidic fuel cell in practical applications.

7.2 Membraneless One-Compartment Direct Hydrogen Peroxide Fuel Cell

Hydrogen peroxide is a carbon-free energy carrier that can be used as both fuel and oxidant in a fuel cell. The whole fuel cell system benefits from the simple design [16, 22]. Hydrogen peroxide can be produced by a two-electron reduction of oxygen, and also by the two-electron oxidation of water which are both plentiful in the environment [102]. Hydrogen peroxide is fairly nontoxic, and can be easily transported in aqueous phase [102]. Unlike fossil fuels, hydrogen peroxide produces water and oxygen through its decomposition or through the redox reactions. In this way, if hydrogen peroxide is produced using natural sources such as wind and solar energy, it can be considered as a green energy carrier [22].

Table 7.1 compares four energy carriers in terms of energy density and cost. Hydrogen peroxide has the lowest cost. Energy density of hydrogen peroxide is comparable to hydrogen but is still lower than methanol. Methanol is not used for fuel cell in very high concentrations. Methanol must be diluted to obtain the

Table 7.1. Free energy, volumetric energy density and energy cost of four energy carriers generated at the fuel cell system.

Fuel	Free energy^(a) (-kJ/mol)	Volumetric energy density (kWh/l)	Fuel cost^(a)	Energy cost^(a) (\$/kW)
Hydrogen	-237	1.83 ^(b)	6.9\$/kg	200
Methanol	-703	4.8	10.2\$/kg	6
H₂O₂	-120	1.45	1.8\$/ton (bulk)	1.84
NaBH₄	-1273	8.70	55\$/kg	10.2

(a) From Sanli and Aytac [103]. (b) Gaseous hydrogen at pressure of 69 MPa.

optimum performance and to control fuel crossover to cathode side. Consequently, the practical volumetric energy density of methanol is much lower than 4.8 kWh/l.

In response to the question if aqueous hydrogen peroxide can be used as a stand-alone energy source [102], two scenarios have been followed. The first scenario revolves around the exploitation of hydrogen peroxide dissolved in alkaline and acidic supporting electrolytes representing fuel (electron donor) and oxidant (electron acceptor), respectively. In such alkaline/acidic bipolar electrolyte, fuel and oxidant should be kept separated in a membrane-based [103] design or in a microfluidic channel [77] where diffusive mixing is limited to a confined liquid-liquid interface. Using 1 M H₂O₂ in 6 M KOH as fuel and 2 M H₂O₂ in 1.5 M H₂SO₄ with Ni/C and Pt/C as catalysts at anode and cathode sides in a Nafion-membrane fuel cell, a power density of 3.75 mW/cm² with a corresponding current density of 14 mA/cm² and a cell potential of 0.55 V was achieved. In a microfluidic fuel cell running on 0.75 M H₂O₂ at Pt electrodes with NaOH/H₂SO₄ electrolytes at a flow rate of 24 μ L/s, a maximum power density of 23 mW/cm² with corresponding current density of 76 mA/cm² and a cell potential of 0.3 V was obtained [77].

There are few issues with using such alkaline/acidic bipolar electrolytes. Firstly, there is a mismatch between the supporting electrolytes of the anolyte and the catholyte. Secondly, precious metals such as Pt are certainly efficient for reduction of H_2O_2 to water, but concurrently they facilitate the direct decomposition of H_2O_2 to oxygen [77, 103, 104]. In addition, it is worth mentioning that the exothermic neutralization of H^+ and OH^- due to diffusive mixing of the reactant and electrolyte consumption [29].

In order to address the above issues, A H_2O_2 system can exploit the one-compartment design using electrodes with different reactivity to oxidation and reduction [22, 23]:

The theoretical electromotive force for the above reactions is 1.09 V which is comparable to the theoretical open-circuit voltage (OCV) of a hydrogen-oxygen fuel cell (1.23 V) and a direct methanol fuel cell (1.21 V).

Yamazaki et al. [16] developed an alkaline fuel cell with a maximum open-circuit potential of 0.13 V using Pt, Pd, Ni and Au wires as selective anode and Ag wire as selective cathode. Yamada et al [22] increased the OCV of the alkaline fuel cell to 0.16 V using Ag-Pb alloy nanoparticles as cathode.

In a recent work, Yamada et al. [23] developed an acidic fuel using an iron phthalocyanine complex as cathode and Ni mesh as anode. Using $[\text{FeIII}(\text{Pc})\text{Cl}]$ as a cathode in an acetate buffer containing 300 mM H_2O_2 (pH = 3), OCV of 0.5 V with a maximum power density of $10 \mu\text{W}/\text{cm}^2$ and a limiting current density of $210 \mu\text{A}/\text{cm}^2$ were achieved. Since H_2O_2 production can be realized under acidic

environment via the two-electron reduction of O_2 using solar energy [22], operation under acidic conditions is highly desirable to establish a hydrogen peroxide-based energy production and storage.

In this chapter, a new one-compartment H_2O_2 fuel cell is proposed using silver (Ag) or nickel (Ni) anodes with ferric ferrocyanide ($Fe_4^{III}[Fe^{II}(CN)_6]_3$) known as Prussian Blue coated on carbon-fiber-based paper as cathode catalyst. Iron (III) atom links to nitrogen, while iron (II) atom links to carbon. Prussian Blue has a basic cubic structure consisting of alternating iron (II) and iron (III) located on a face centered cubic lattice [105]. Prussian Blue is widely available and very cost effective compared to precious metals. Prussian Blue (PB) is a renowned catalyst for H_2O_2 reduction under acidic conditions and its electrocatalytic reduction of hydrogen peroxide for biosensing and analytical applications has been studied extensively [105, 106].

7.2.1 Preparation of Prussian Blue (PB)

The procedure of chemical preparation of PB was adopted from Ref. [104]. In order to prepare Prussian Blue, the required amount of 0.5 M $FeCl_3$ (Sigma-Aldrich) in 0.1 M HCl (Sigma-Aldrich) was added drop wise to a solution of $K_3[Fe(CN)_6]$ from Sigma-Aldrich in 0.1 M HCl at room temperature. The immediate formation of dark blue colloid was observed. The solution was stirred for 1 hour. The produced PB was collected by filtration through a PTFE filter with an average pore size of 0.22 μm from Wattman. The collected PB was washed with 0.1 M HCl until the filtrate become colorless. PB was removed from the filter and kept in an oven at 100 $^{\circ}C$ for 3 hours.

To make PB supported on carbon, the required amount of Vulcan XC-72 was suspended in 0.1 M HCl and agitated in an ultrasound water bath. The required

Figure 7.1 Powder X-ray diffraction (XRD) patterns for carbon-supported and (b) unsupported Prussian Blue.

amount of $K_3[Fe(CN)_6]$ in 0.1 M HCl and 0.5 M $FeCl_3$ from in 0.1 M HCl were added drop-wise to the carbon slurry, respectively. The remaining procedure was the same as above.

Both unsupported and carbon-supported synthesized PB samples were analyzed using a powder X-ray diffraction (XRD) system (PANalytical®, Netherlands). Applied potential and current were 40 kV and 40 mA with a scan speed of 0.067 degree/second and a step size of 0.02 degree. As shown in Figure 7.1, the diffraction patterns showed pronounced peaks at $2\theta = 17.4^\circ$, $2\theta = 24.6^\circ$, $2\theta = 35.2^\circ$ and $2\theta = 39.4^\circ$, respectively, corresponding to $Fe_4[Fe(CN)_6]_3 \cdot xH_2O$ [104]. The XRD peaks for both carbon-supported and unsupported PB remained

identical indicating that the modification process does not affect the structure of PB. There was also no reaction between PB and carbon.

7.2.2 Electrochemical Characterization of Prussian Blue

The electrocatalytic reduction of H_2O_2 over Prussian Blue was examined in a three-electrode cell with a rotating ring-disk glassy carbon electrode. Small portions of unsupported and carbon-supported PB solution containing Nafion ($2\ \mu\text{l}$) were placed on the glassy carbon electrode with a diameter of 4 mm and dried under an incandescent light bulb for 30 minutes. The preparation of the catalyst solution follows the same procedure reported in Section 7.2.1. Figure 7.2 shows the cyclic voltammetry (CV) results of H_2O_2 in a supporting electrolyte of 0.1 M HCl (pH=1) containing 0.5 M H_2O_2 . Cyclic voltammogram of the unsupported PB in 0.5 M HCl solution in the absence of H_2O_2 indicates that there is no specific catalytic current of H_2O_2 reduction in the cathodic sweep. Cyclic voltammograms of unsupported PB in the presence of H_2O_2 demonstrated smooth trends at all rotating speeds. In the characterization experiments of carbon-supported PB over the rotating ring-disk glassy carbon electrode in the presence of H_2O_2 , rapid bubble formation was observed before the CV test. Large fluctuations were observed in the cyclic voltammogram of the carbon-supported PB in the presence of H_2O_2 due to mass transport limitation. Rapid emergence of bubble, even at high rotating speed of 2500 rpm is caused by the quick decomposition of H_2O_2 to oxygen and water in the presence of carbon particles.

The onset potential of H_2O_2 reduction under acidic condition on the glassy carbon electrode with PB is 0.6 V. In order to have selective electrodes, the onset potential for H_2O_2 oxidation on an electrode of interest should be lower than that of H_2O_2 reduction over PB. For example, the onset potential of H_2O_2 oxidation on

Figure 7.2 Cyclic voltammograms of H_2O_2 on glassy carbon electrode modified by unsupported PB. The measurements were performed in an aqueous electrolyte of 0.1 M HCl containing 0.5 M H_2O_2 . Scan rate of 10 m/s was selected.

a nickel (Ni) electrode and on a silver (Ag) electrode in alkaline medium were *ca.* -0.09 and *ca.* -0.11 V [16]. These values are lower than 0.6 V. Therefore, Ni and Ag electrodes were selected as potential anodes. Since PB is not stable under alkaline conditions, the selectivity of Ni and Ag electrodes compared to PB should be examined in an acidic medium.

7.2.3 Fabrication of the One-compartment Fuel Cell

PB coated electrodes were prepared by spraying a solution of PB containing Nafion on a piece of carbon paper (HGP-H 90 from Toray). The solution was made by adding 4 ml Isopropanol and 1.2 ml DI water from Millipore (Direct Q) to 24 mg of PB. The solution was agitated in an ultrasound water bath for 30 minutes. Subsequently, 100 μl of Nafion with a concentration of 5% was added to

the solution and agitated for 30 minutes. Nafion was used as a binder while the deposited PB catalyst ink over the glassy electrode without Nafion content was washed easily from the surface of the electrode.

The resultant solution was sprayed on a piece of carbon-fiber-based paper (HGP-H 90 from Toray) using a painting gun (Badger model 100 LG), connected to a regulator to reduce the supplied gas pressure. The spraying process was done under the light of an incandescent light bulb to facilitate the evaporation of water and isopropanol from the carbon paper. To make a catalyst layer with a uniform loading of ca. 10 mg/cm^2 over the carbon paper, frequent spraying with subsequent drying under the light was repeated until the whole solution was sprayed on the carbon paper.

Silver anode was made of a thin silver plate from Sigma-Aldrich while nickel anode was a metallic mesh. Anode and cathode were immersed in a solution of $0.5 \text{ M H}_2\text{O}_2$ with a supporting electrolyte of 0.1 M HCl , Figure 7.3. Electrodes

Figure 7.3. A schematic figure of one-compartment fuel cell running on H_2O_2 as both fuel and oxidant. Supporting electrolyte is 0.1 M HCl dissolved in $0.5 \text{ M H}_2\text{O}_2$. Anode comprises of a silver foil or a nickel mesh. Cathode is made of Prussian blue coated on carbon paper.

were connected to an electric load system (PGSTAT 302 with GPES Manager as interface software) using alligator clips. A potential scanning rate of 10 mV/s and a potential step of 10 mV was set. The characterization was carried out at room temperature of 25°C.

7.3 Results and Discussions

For all fabricated cells, the open-circuit potential (OCV) was monitored for 5 minutes. As shown in Figure 7.4, the fuel cell with nickel anode showed an OCV of 0.60 V which degraded slowly. Silver produced a stable OCV of 0.53 V. These results are superior to the maximum OCV reported previously for both acidic and alkaline mediums in a single-compartment fuel cell running on H_2O_2 [16, 22, 23]. The maximum OCV in acid condition reported previously is 0.5 V using nickel anode and $[\text{Fe}^{\text{III}}(\text{Pc})\text{Cl}]$ cathode [23].

Linear potential sweep voltammetry with a scan rate of 10 mV/s was carried out to examine the potential-current characteristic of the single-compartment fuel cell. As shown in Figure 7.5, the fuel cell represents a maximum power density of ca. 0.8 mW/cm^2 at 0.3 V with silver anode and a maximum power density of ca. 1.55 mW/cm^2 at 0.3 V with nickel anode. These results are two orders of magnitude higher than the best results reported in the literature which is $10 \text{ }\mu\text{W/cm}^2$ [23]. In addition, PB coated on carbon paper is very stable in acidic condition which is compatible to H_2O_2 production through the electrochemical two-electron reduction of O_2 that requires highly acidic conditions [22]. No leaching of the PB was observed.

Figure 7.4 Open-circuit potential of the single-compartment H_2O_2 fuel cell with nickel and silver anodes and unsupported PB coated on carbon paper as cathode. Tests were done under acidic condition using 0.1 M HCl and 0.5 M H_2O_2 .

Figure 7.5 Current-potential and current-power curves of the single-compartment H_2O_2 fuel cell with nickel and silver anodes with unsupported PB coated on carbon paper as cathode. Performance tests were carried out under acidic condition using 0.1 M HCl and 0.5 M H_2O_2 .

In order to investigate the stability of the fuel cell, a chronoamperometry test at 0.2 V was carried out. As observed in Figure 7.6, fuel cell with nickel anode was able to generate a higher current at the beginning of the test which is in agreement with the results from Figure 7.5. In contrast to a silver anode, a slow degradation in the performance was observed. At the current operating conditions (pH, catalyst loading, anode materials, and H_2O_2 concentration), silver anode may show a more stable long term performance. However, to have a fair comparison, the effect of the flat planar surface of the silver anode and the mesh structure of the nickel anode must be considered for future investigations.

Figure 7.7 shows individual anodic and cathodic polarization curves obtained versus an external Ag/AgCl reference electrode. This plot reveals that silver anode contributes more to limiting the overall fuel cell performance. This

Figure 7.6 Chronoamperometry test at cell potential of 0.2 V. Performance tests were carried out under acidic condition using 0.1 M HCl and 0.5 M H_2O_2 .

may be associated with the electrochemical kinetics and mass transport. Since no significant mass transport limitation was observed in Figure 7.7, the main

Figure 7.7 Steady-state anodic and cathodic polarization data for the single-compartment fuel cell measured in situ at room temperature under chronoamperometry control, using a platinum electrode as counter electrode and an external Ag/AgCl reference electrode.

contribution may be related to the electrochemical kinetics. In this case, there is a huge potential for further improvements of catalyst selection.

7.4 Conclusions

A high performance membraneless H_2O_2 fuel cell using Prussian Blue as cathode and silver and nickel as anode materials in an acidic medium was realized. Open-circuit potential and maximum power density is improved significantly compared to the past results reported in the literature. The current design provides a strong platform for further developments. Prussian Blue is highly stable in acidic environment and has a high electroactivity towards the reduction of H_2O_2 . In the future, other materials can be explored for lower anode overpotential. The current fuel cell design is suitable for on-chip power generation schemes such as powering portable lab-on-chip devices [107] and off-the grid micro sensors. Fuel crossover and mixing of fuel and oxidant is not an issue in this

design. Unlike conventional microfluidic fuel cells, continuous streams of fuel and oxidant are not required to keep the fuel separated from the oxidant

Chapter 8 Conclusions and Future Work

8.1 Summary of Accomplishments

There is a clear need for the development of power sources that can operate for a long time. Micro fuel cells can be used as a recharger for secondary batteries of micro devices to increase their operation time. They can take advantage of fuels with high energy density. Since a fuel cell is considered as an engine to convert chemical energy of a fuel and an oxidant to electrical energy through electrochemical reactions, its design is more complex compared to electrochemical energy storage such as a battery. In order to keep a fuel cell operating continuously for a long time, many functionalities must be met. A fuel cell system comprises of some auxiliary components and a fuel cell engine. In order to use a fuel cell for an application with limited space, the whole fuel cell system should be miniaturized. Such miniaturization efforts have been done and widely reported. However, the implementation and integration of micro fuel cells in practical applications require further research and development.

The focus of this doctoral thesis has been mainly the development of two platforms of one-compartment fuel cells which have less design constraints compared to the conventional two-compartment fuel cells.

In the first platform, an air-breathing microfluidic fuel cell was the main focus. The corresponding research activities are listed as following:

- **Numerical simulation of physico-chemical processes within the cell**

A numerical model to simulate transport phenomena and electrochemical reactions of a customized fuel cell was established. The effect of flow architecture was investigated. Better understanding of phenomena affecting the overall fuel cell performance was obtained.

- **Detailed characterization of an air-breathing microfluidic fuel cell with flow-over and flow-through anodes**

Effect of flow architecture and fuel concentration on the overall fuel cell performance was studied. Using flow-through anode improves the fuel utilization. Long term operation was investigated for both flow architectures and different fuel concentrations. Chronoamperometry results demonstrated that flow architecture has a significant impact on the overall cell performance. Bubble formation in the fluidic channel due to electrooxidation of formic acid at the anode was the main issue limiting the fuel cell performance.

- **Investigation of the air-breathing microfluidic fuel cell with fuel reservoir**

In order to address the issue of bubble formation in conventional design of air-breathing microfluidic fuel cells, a novel design with a fuel reservoir above the anode was investigated. Bubbles were formed in the reservoir and do not affect the cell performance. In addition, this design is able to use fuel of high concentrations. The mass transport to anode side was improved.

In the second platform, research activities revolved around a single compartment fuel cell with selective electrode:

- **A proof-of-concept membraneless single-compartment fuel cell using hydrogen peroxide as both fuel and oxidant with Prussian Blue as cathode material**

Performance of this single-compartment fuel cell was characterized. Superior performance was observed compared to the results reported in the literature. The results are very promising and may open a new avenue for making a new generation of micro power generators.

8.2 Future Directions

Some future research work directions have been suggested in the conclusion section of each chapter. This thesis potentially opens new research directions for the development of micro fuel cells. In order to use a microfluidic fuel cell as a power generator, sufficient durability and high system integration with a power consumer must be considered. Thus, future research activities may include the following topics:

- In the case of using hydrocarbon fuels such as methanol or formic acid, bubble formation in the fuel cell can be an issue at high current densities. Bubble dynamics plays a critical role in mass transport of the fuel to electrocatalytic active sites. *In-situ* analysis of bubble formation over anode electrode shed light on better hydrodynamic manipulation of streams in the fluidic channel. Despite the previous investigations [78, 108], it is still not clear how bubbles are nucleated and grow over a catalytic surface or dissolved in a microfluidic channel. In addition, a numerical simulation of physicochemical processes including two-phase flow analysis is very critical for a microfluidic fuel cell and has not been reported.

- A detailed analysis of the fuel cell with fuel reservoir is needed. Effect of varying electrolyte flow rate, channel depth and length, fuel concentration and applied pressure need to be investigated in details. Different fuels and alkaline electrolytes can be explored. A numerical simulation would provide further insights into fuel and oxygen consumption as well as fuel/electrolyte interface.
- There are a number of research activities on material selection and synthesis for membraneless one-compartment hydrogen peroxide fuel cell. An improved power density should potentially lead to a huge market with niche applications such as sensors connected in a wireless network for environmental monitoring and micro robots. New materials with lower activation overpotentials must be explored especially for the anode side. There are many key questions about the effect of temperature, pH, H_2O_2 concentration and catalyst structure on the kinetics and rate of the redox reactions. In addition, a detailed study on half-cell reactions is needed for a better understanding of the fuel cell mixed potential. From the physical chemistry point of view, fundamental studies can be carried out on new catalysts synthesis to increase the overall performance and long term operation.

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