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Air-Breathing Membraneless Laminar Flow-Based Fuel Cell with Flow-Through Anode

Seyed Ali Mousavi Shaegh, Nam-Trung Nguyen, Siew Hwa Chan, Weijiang Zhou

School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

Energy Research Institute at NTU (ERI@N), Singapore 637553, Singapore

Abstract

This paper describes a detailed characterization of laminar flow-based fuel cell (LFFC) with air-breathing cathode for performance (fuel utilization and power density). The effect of flow-over and flow-through anode architectures, as well as operating conditions such as different fuel flow rates and concentrations on the performance of LFFCs was investigated. Formic acid with concentrations of 0.5 M and 1 M in a 0.5 M sulfuric acid solution as supporting electrolyte were exploited with varying flow rates of 20, 50, 100 and 200 µl/min. Because of the improved mass transport to catalytic active sites, the flow-through anode showed improved maximum power density and fuel utilization per single pass compared to flow-over planar anode. Running on 200 µl/min of 1 M formic acid, maximum power densities of 26.5 mW/cm² and 19.4 mW/cm² were obtained for the cells with flow-through and flow-over anodes, respectively. In addition, chronoamperometry experiment at flow rate of 100 µl/min with fuel concentrations of 0.5 M and 1 M revealed average current densities of 34.2 mA/cm² and 52.3 mA/cm² with average fuel utilization of 16.3 % and 21.4 % respectively for flow-through design. The flow-over design had the corresponding values of 25.1 mA/cm² and 35.5 mA/cm² with fuel utilization of 11.1% and 15.7% for the same fuel concentrations and flow rate.

Keywords: Fuel cell, membraneless fuel cell, microfluidic fuel cell, laminar flow, flow-through architecture, fuel utilization.
1. Introduction

The emergence of portable microelectronic devices and off-the-grid sensors employed for biological, environmental and security monitoring leads to the high demand for miniaturized and reliable power sources. For such applications, having miniaturized high-energy-density power sources to provide long-term operation is a critical requirement. Micro fuel cell (MFC) technology can take advantage of fuels with energy densities of an order of magnitude higher than the energy stored in batteries [1]. MFC can be used to make a hybrid system in connection with a secondary battery to increase the battery life span.

To harvest the high energy density of fuels, the miniaturization and integration of fuel cell systems are inevitable. The 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 with passive and self-regulating fuel/oxidant delivery schemes. Different components of a MFC engine should be fabricated in a monolithic manner in connection with fuel and oxidant delivery systems. Some miniaturization and integration activities for MFCs include the development of monolithic structure with integrated electrodes and membrane on porous silicon with minimum membrane humidity conditioning and high proton conductivity [2], microreactors for hydrogen production from methanol [3], self-regulating hydrogen generator from metal hydrides [1, 4], passive or self-circulation fuel/oxidant delivery and built-in CO₂ bubble removal system [5-7].

Membraneless laminar flow-based fuel cell (LFFC) [8], known as microfluidic fuel cell [9] or membraneless fuel cell [10], is an attempt that aims to simplify the design and fabrication of MFCs for higher level of integration. LFFCs take advantage of the lamination of streams including fuel and oxidant reactants with 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 (MECR). 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 [11].

Different designs and development efforts of LFFCs were reviewed in [9], and a recent review article [8]. Similar to membrane-based fuel cells, the performance of LFFCs is limited by the combined effect of activation, Ohmic and mass-transport losses. Because of the laminar flow regime in the channel, mass-transport losses can significantly affect the
performance of the fuel cell. For a given fuel-electrolyte-oxidant combination, these losses can be generally modified by flow architecture within the cell which is determined by the design of catalyst-reactant interface, electrodes configuration, and channel geometry [8] as shown in Figure 1. In primary designs of LFFCs, the performance was dominated by low concentration of dissolved oxygen-based oxidants [12]. By exploiting higher-quality oxidant such as hydrogen peroxide [13], or introducing air-breathing gas-diffusion electrode as a cathode [14, 15], cell current densities increased from 0.1s mA/cm² to 100s mA/cm² [8].

As shown in Figure 2 Error! Reference source not found. and Figure 3, to avoid direct contact of fuel stream to the cathode, a blank electrolyte stream is required which demands a separate electrolyte reservoir. Therefore, two reservoirs are needed for fuel and electrolyte streams. Compared with a both-aqueous fuel and oxidant cell, the development practices for air-breathing LFFCs are less complicated since there is one reactant stream in the channel. LFFCs with an air-breathing cathode can take advantage of the high concentration of oxygen in air, 10 mM, and the higher diffusion coefficient of oxygen in air, 0.2 cm² s⁻¹, as compared to the respective values in aqueous media of 2–4 mM and 2 × 10⁻⁵ cm² s⁻¹ [14]. Using Ag/AgCl reference electrode to obtain the anodic and cathodic potentials revealed that unlike the LFFCs based on oxygen-based oxidants, oxygen concentration is not the source of limiting performance for an air-breathing LFFC [16].

Numerical simulation for a LFFC with an air-breathing cathode showed that a uniform concentration of oxygen is provided for a gas-diffusion electrode. But a depletion boundary layer is easily formed over the planar flow-over anode [17]. Due to the laminar nature of the streams, 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 electrode can’t be replenished, and reactant concentration drops gradually along the anode. Therefore, only a part of the electrode contributes to current generation [17, 18]. In addition, the fuel in the middle of the channel passes through the channel without being used which decreases fuel utilization.

For designs with both aqueous fuel and oxidant streams, few approaches were proposed to provide a uniform concentration of reactants over electrodes. Fuel flow rate can be increased to supply higher amount of reactant to the electrodes [17]. In this case, maximum power density can be increased but fuel utilization drops, and the performance optimization is a trade-off between power density and fuel utilization. Yoon et al. [19] manipulated the
depletion boundary layer by adding fresh reactants through multiple inlets or removing the depleted zone through multiple outlets along the reactive surfaces as shown in Figure 1(c). In another approach, Yoon et al. [19] could improve the current density up to 40% by implementing micro ridges on the bottom wall of the channel. Such micro ridges can create transverse flow across the channel to transport the reactants from the middle of the channel to the reactive areas on side walls. This approach can increase the mixing of co-laminar streams through the channel with the resulting parasitic effects of fuel crossover. Xuan et al. [20] in a CFD/electrochemical model, addressed this issue by incorporating micro ridges in a two-compartment counter-flow LFFC. Results showed chaotic flow inside the channel with reactive areas enables the LFFC to improve fuel utilization and maximum power density. But at high current densities, cell potential drop rapidly because of the longer route of charge transport between the electrodes compared with co-laminar compartment.

In another approach for a LFFC with both aqueous fuel and oxidant, fuel utilization was enhanced by exploiting the full-depth of flow-through electrodes in a sequential [21] or a cross-over flow architecture as shown schematically in Figure 1 (d) [21-23]. While the whole fuel and oxidant streams can flow through the electrodes, three-dimensional electrode architecture improves the utilization of the reactive areas inside the porous electrodes. Using this concept, Kjeang et al. [23] could achieved fuel utilization of 94% at flow rate of 1 µl/min and produced 20 mW/cm² at 0.8 V in an all-vanadium (V²⁺/V³⁺ and VO²⁺/VO²⁺) microfluidic fuel cell.

Fuel utilization can be optimized by breaking the trade-off between fuel utilization and power density using the hydrodynamic focusing [18, 24]. Jayashree et al. [18] could improve the fuel utilization in LFFCs with air-breathing cathode by hydrodynamically focusing the fuel stream to a thin layer on the anode. The fuel layer is just adjusted by the flow rate ratio between the fuel and the electrolyte streams [18]. Fuel utilization of up to 40% was achieved using fuel-to-electrolyte ratio of 1:20 and total flow rate of 100 µl/min. This approach decreases the amount of fuel passes through the channel without reacting, however, it adds complexity to fluidic design of the whole system.

For practical applications, the fuel cell system must benefit from high energy density which dictates high fuel utilization per single pass or integration a recirculation system with fuel cell. Hollinger et al. [15] proposed the implementation of a nanoporous tracketech separator at
the interface of methanol as fuel and the electrolyte stream which decreased fuel crossover to the cathode side. This scheme may facilitate the integration of a recirculation system for fuel stream.

In this work we demonstrated the design, fabrication and characterization of an air-breathing LFFC combined with a flow-through anode to explore the impact of anodic flow architecture on the performance and the fuel utilization per single pass. In an analogy with Yoon et al. work [19] which has three fuel inlets [19], present flow-through anode has accommodated infinite fuel entry points in an uncomplicated design. To have a benchmark for comparison, an air-breathing LFFC with a planar flow-over anode was also fabricated at similar dimensions using the same materials.

Carbon dioxide is a product of formic acid or methanol electrooxidation, and at high current densities bubbles may form in the channel. Bubble dynamics influence local species transport and liquid-liquid mixing and crossover [25], and its effect on cell performance becomes significant as flow rate decreases. While the investigations available in the literature usually exploited fuel rates of 300 µl/min and higher [14, 15, 26] for characterization, this study attempted to explore the performance and fuel utilization per single pass at medium to low flow rates, less than 200 µl/min, to increase the overall energy density of the system. 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 and 1 M formic acid with 0.5 M sulfuric acid as supporting electrolyte.

2. Fabrication

Both planar and flow-through designs were fabricated from the same materials with the same geometrical dimensions unless stated otherwise. Anode is made of plain Toray carbon-fiber-based paper with a typical thickness of 280 µm and a porosity of approximately 78%. This carbon paper is 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 7-8 mg/cm². 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/cm² to improve the Pd particles dispersion. Nafion solution with a loading of 3 mg/cm² is used as a binder. To have a low-viscosity ink, isopropanol is added to
the mixture followed by ultrasound sonication for 1 hour. Ink is spread over a piece of carbon paper with a size of 10×10 cm² manually and dried under a fume hood for 20 minutes and subsequently kept in an oven at a temperature of 80 °C for 1 hour.

As shown in Figure 2, the anode strip was cut in a size of 3×30 mm² for the planar design. A groove with the same size of 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 represents as a current collector.

To enable the fuel to pass through the anode, a slit was machined through the graphite current collector. This flow configuration allows the fuel stream to enter to the top channel as shown in Figure 3. For the flow-through design, the anode strip was cut in a size of 5×32 mm². Since strip was fixed on the edges of the slit using conductive epoxy containing silver particles (CircuitWorks® Conductive Epoxy from Chemtronics®), an electrode with final active area of 3×30 mm² was produced. Therefore, both designs benefit from the same anodic electrocatalytic active area of 0.9 cm².

The main flow channel was made of poly(methyl methacrylate) (PMMA) with a thickness of 1.5 mm from Margacipta® which was resistant to sulfuric acid and formic acid at room temperatures. The volume of the channel in both designs is 135 microliters. Fluidic channels were cut through or engraved in PMMA using a CO₂ laser machining system (Universal M-300 Laser Platform, Universal Laser Systems Inc.). 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 65 µl while another half of the channel is filled only with supporting electrolyte.

In order to provide consistent results, commercial cathode with main application for direct methanol fuel cell made of carbon-fiber-based paper from Alfa-Aesar was used. In this case, Teflon® content of the cathode is high enough to prevent the leakage from the channel through the gas-diffusion electrode. The cathode was attached to the top of the channel using a double-sided adhesive layer. A stainless steel mesh as a current collector was placed on the cathode using a paper clip. Alligator clips connected this metallic mesh to the external circuit.

Both electrodes were aligned with the channel to maintain 0.9 cm² anodic and cathodic catalytically-active surface area. Double-sided adhesive layer was used to attach the channel
to the graphite plate which accommodated anode. Fluidic interconnects for handling inlets and outlets were glued to the PMMA or graphite by fast drying epoxy. The fabricated cell was inspected for leakage using DI water from Millipore. Figure 4 depicts the assembled cell.

3. Characterization

The generation of electricity in the LFFC follows the electrochemical reactions at the anode and the cathode. The oxidation reaction of formic acid over platinum-group metals can follow two pathways: (i) dehydrogenation pathway which is the direct and favorite path for generating active species of $\text{H}^+$ and releases electrons; and (ii) dehydration pathway with poisoning intermediates which blocks the active sites for direct pathway. Direct pathway of formic acid oxidation is shown in equation (1):

$$\text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^- \quad E^\circ = -0.199 \text{ V vs SHE}$$

Palladium (Pd) has the tendency to break 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 [27]. Protons travel across the channel by diffusive transport due to a gradient in proton concentration between the anode and the cathode, and by electromigration due to the voltage gradient between the electrodes [8].

Oxygen is supplied through the gas-diffusion cathode from the ambient air. Without considering different reaction intermediates, oxygen reduction reaction (ORR) is occurred as:

$$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad E^\circ = 1.229 \text{ V vs SHE}$$

As shown in Figure 2 and Figure 3, both flow-over and flow-through designs of LFFCs were characterized on a fuel stream with 0.5 M and 1 M formic acid and 0.5 M sulfuric acid as supportive electrolyte and a stream of 0.5 M sulfuric acid as the electrolyte stream to avoid direct contact of fuel to cathode. The flow rate of the fuel and the electrolyte streams were kept constant at a fixed fuel to electrolyte ratio of 1:1. The fuel cells were tested with the fuel flow rates of 20, 50, 100 and 200 µl/min. Both fuel and electrolyte streams were delivered by a syringe pump (KD Scientific). To receive reproducible results, the following procedure was applied. Prior to running the experiment at any given flow rate, the syringe pump was driven for a specific period of time, from 5 minutes at 200 µl/min to 20 minutes at 20 µl/min. This
step guarantees 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 experimentation. A potential scanning rate of 5 mV/s with a potential step of 0.01 V were selected to provide sufficient occasion to capture the effects of active mechanisms inside the cell such as CO₂ generation.

The characterization 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).

The main objective of this investigation revolved around the effect of flow architecture on the fuel cell performance which mostly affects the mass-transport losses. In order to make direct comparisons, it was aimed that two designs would be 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 µl/min. Frequency range of EIS was 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 determines the total cell resistance of 2.03±0.33 Ω and 1.83±0.32 Ω for planar and flow-through designs, respectively. These values reveal the performance characteristic of both fuel cell designs have almost the same Ohmic losses. In OCV condition, there is no disturbance in the channel, for instance bubble generation due to current generation, to alter the fluidic lamination of two streams or change the cross-sectional area of charge transport in the channel from anode to cathode. For all fabricated cells, the open circuit potential (OCV) was monitored for 10 to 20 minutes – depending on the flow rate – before the experimentation to examine the stable liquid-liquid interface in the main channel.

4. Results and discussions
4.1 Optimum running flow rate

To find the optimum range of flow rate that produces maximum power density, linear sweep voltammetry for both designs were carried out and the corresponding power densities were calculated. As shown in Figure 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 µl/min to 400 µl/min. For the flow rates lower than 200 µl/min, the maximum power density reduces dramatically as flow rate decreases. Therefore, flow rates of 200 µl/min, 100 µl/min,
50 µl/min, 20 µl/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/cm² is lower than the maximum power density of 26 mW/cm² in an air-breathing design with planar anode at 300 µl/min [14]. But at lower flow rate of 100 µl/min, the present maximum power density of 18 mW/cm² is much higher than 10 mW/cm² from Ref. [14]. Their cell had a channel height of 2 mm, anode length of 20.5 mm and total active area of 0.62 cm² with 10 mg/cm² of Pd catalyst particles on graphite plate. These differences can be associated with the usage of catalyst-covered carbon paper as anode and the channel dimensions in the present study.

4.2 Fuel cell performance with 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 Figure 6 and Figure 7. There are a few observations worth mentioning. Three distinctive regions with dominant losses of activation, Ohmic and mass-transport are obvious for both designs. As flow rate decreases, the OCV drops mainly because of the widening inter-diffusion region between the fuel and the electrolyte streams and the resulting mixed potential over 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, with Peclet number of 880, flow-over design has a maximum power density and current density (limiting current density) of 19.4 mW/cm² and 90 mA/cm² while the flow-through design has the corresponding values of 26.5 mW/cm² and 120 mA/cm². The maximum power density of planar design for flow rates of 200, 100, 50 and 20 µl/min are 19.4±4.34, 17.9±5.34, 14±3.34 and 9.87±3.54 mW/cm² compared to 26.5±4.2, 19.8±4.25, 13.4±1.84 and 11.4±1.197 mW/cm². Along with the data shown in Figure 5, these results provide an evidence for the development of mass transport in fuel cell with flow-through anode. Higher power densities of flow-through design are mainly related to fast replenishments of used reactants by fresh ones. 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. However the flow-over anode was made of porous carbon paper, but numerical simulation revealed that full-depth of the anode can’t have contribution in current generation because of the lack of advective mass transport through the anode. Also, due to the growth of depletion boundary layer over flow-over anode, only the first few millimeters of the electrode
benefit from high fuel concentration [17]. For both designs, mass-transport losses became significant at potentials lower than 0.4 V for all flow rates, except flow rate of 200 µl/min. Accumulation of reaction products, mainly CO₂, and slow replenishment of depletion boundary layer can be the major reasons for mass-transport losses.

Buildup of carbon dioxide over the anode may result in bubble generation. Carbon dioxide bubbles generated in the channel can create two main problems [28]. Firstly, they can fill the channel and change the interface of the two streams, or even mix up the two streams completely, which results in a crossover phenomenon. Mixing of fuel with electrolyte stream, causes parasitic current and decrease the cell current [29]. Secondly, bubbles block the active sites for fuel oxidation and effective area of anode reduces. Periodic growth and detachment of bubbles within the channel brings about a discontinuous flow field along the channel, which finally leads to an unstable fuel cell operation.

4.3 Fuel cell performance with 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 8 and Figure 9, the OCV of both designs at lower flow rates of 20 and 50 µl/min are slightly higher compared to the results from 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, maximum power density for planar design is lower than the corresponding value of flow-through design. Maximum power densities at flow rates of 200, 100, 50 and 20 µl/min are 17.8±1.38, 17.5±1.34, 16.1±1.73 and 7.70±0.52 mW/cm², 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/cm².

Sharp drop of potential in Figure 8 compared with Figure 9 at low flow rates of 20 and 50 µl/min is highly associated with the slow local transport of species to active sites and sluggish removal of carbon dioxide from catalytic areas. In the very low flow rate regime, the fuel cell power generation is dominated by diffusion transport from the bulk [30].
Running the cell on 50 µl/min of formic acid shows a Columbic fuel utilization of 43±3% per single pass calculated by equation (2) at the point of maximum power density for both planar and flow-through designs:

\[ \varepsilon_{\text{fuel}} = \frac{J}{nFv_{\text{fuel}}} \]  

(2)

where, \( J \) is the generated current by the cell and \( v_{\text{fuel}} \) represents the rate at which fuel is supplied to the fuel cell with unit of mol/sec.

As shown in Figure 10(a), current at cell potential of 0.4 V decreases as flow rate decrease. At each flow rate, four different tests show similar trend, however, results of experimentation with 1 M formic acid shows a slight improvement compared to 0.5 M formic acid. For the planar design at a flow rate of 200 µl/min with concentration of 1 M formic acid, the average current and the associated fuel utilization is 41.4±5.63 mA and 6.31±1.1% while for the same design at flow rate of 50 µl/min with 1 M formic acid, the current and fuel utilization are 32.0±4.9 mA and 49.9±8.2 %. In this case, the amount of fuel introduced into the channel decreases 400%, but the current shows a drop of 22%. Two conclusions may be drawn here. Firstly, it indicates that the number of available sites for electrooxidation is far lower than the required ones. Secondly, residence time of fuel at the vicinity of catalytic active area may play a critical role [31]. As the flow rate decreases to 50 µl/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.

4.4 Long term performance

For the aforementioned experiments, 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 experimentation. Therefore, potential sweep voltammetry represents a complicated and time-dependent function of a large number of coupled physical and chemical parameters. In this case, recognition the effect of one individual phenomenon or effect on the cell performance becomes very difficult and in some cases even impossible.

To distinguish the effect of flow architecture on the cell performance, long term performance test (chronoamperometry experiment) was carried out at flow rate of 100 µl/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 reduce performance degradation because of catalyst carbon monoxide (CO) poisoning, newly fabricated cells were used for long term performance at cell voltage of 0.4 V where the maximum power density was monitored. A rapid degradation in current generation was observed probably due to the formation of CO poisoning intermediates. To capture the effect of flow architecture on the long term performance of the fuel cell, new experiments were carried out on cell potential of 0.2 V. At this cell potential, anode has higher overpotential which facilitates the oxidation of CO. Therefore a more stable performance was observed.

As show in Figure 11(b), operating at two fuel concentrations of 0.5 M and 1 M, flow-through design has a higher average current density of 34.2±2.69 mA/cm² and 52.3±14.1 mA/cm² 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 with 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 planar anode (35.47 mA/cm²) while running on 1 M formic acid at fuel flow rate of 100 µl/min.

As a comparison, improvements in maximum power density and fuel utilization for the cell with flow-through electrodes was reported for an all-vanadium microfluidic fuel cell [23], however, the electrochemical kinetics of this cell is totally different from the current study.

The improved cell current indicates that flow-through anode can exploit more amount of fuel for electrooxidation reaction. Since fuel is introduced to the channel through the electrode, the depletion boundary layer is replenished effectively. In addition, unlike the planar design, more fuel molecules get the chance to come into contact with the catalytic active area. In a planar design, the fuel volume in the middle of the channel, where the interface is formed, just passes through the channel without getting a chance to interact with the catalyst layer.
For all four set of experiments, a gradual current degradation was observed. The degradation is associated with CO poisoning of anode catalyst and accumulation of CO$_2$ on the catalytic active sites. The fluctuations may be related to intermittent feeding fresh reactant to the active sites because of the CO$_2$ formation as a product of formic acid electrooxidation.

The solubility of CO$_2$ in water at room temperature is 178 mg/100 ml [8] which is equivalent to 0.0404 M. If it is assumed that carbon dioxide and protons are the only products of the formic acid electro oxidation, the concentration of 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 total flow rate of 200 µl/min (with average current density of 34.2 mA/cm$^2$) 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 because of the current generation. As a result, the fluctuations in current (green curve) are not significant. If the amount of CO$_2$ generated in the channel is beyond the saturation threshold, bubbles start to emerge in the channel. Therefore, the observed fluctuations in Figure 11(a), for other three curves with higher current densities that 34.2 mA/cm$^2$, can be associated to the emerging bubbles in the channel. Bubbles can be pushed to the outlet by the drag force of liquid running in the channel.

As observed for Figure 6 to Figure 9, generally some fluctuations for current densities higher than 40 mA/cm$^2$, were observed, mostly because of the reactions products. Since, flow-through design has the ability to use more portion of fuel, the chance of bubble generation in higher. However, at high flow rates bubbles formed in the channel could detach from the anode and channel wall and wash away towards the outlet. But at a moderate flow rate, bubbles could attach the channel walls and trap the channel partially. This can block the anode active sites and reduce the current generation. Therefore, the partial channel block may change very much the range of 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.

5. Conclusions
In this work, performance of two air-breathing laminar flow-based fuel cells running on formic acid with flow-over and flow-through anode architectures was presented. To explore the impact of flow architecture on the performance, medium to low flow rates of fuel and electrolyte were utilized. 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 higher fraction of the fuel introduced to the channel compared to flow-over anode, however, the flow-through design may experience higher pressure drop.

For practical applications, air-breathing fuel cell should be able to operate at medium to low flow rates with high power density and fuel utilization. In case of using formic acid and methanol which are widely available and stable in high concentrations, CO₂ bubble generation at high current densities plays a very effective role. In one hand, operation at low flow rates while high power density can be achieved is a desired requirement, but on the other hand, removal of reaction products and bubbles from the active sites become difficult as flow rate decreases. Breaking this trade-off needs a different solution for air-breathing LFFCs. Experimental investigations and numerical simulations on reaction products over anode and cathode reaction with considering bubble formation in the channel provide helpful insights into the performance determining parameters.

For practical long-term operations, fuel cell 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 catalyst particles.

6. References


List of Figures

**Figure 1:** Membraneless Laminar Flow-Based Fuel Cell, (a) Schematic sketch of membraneless LFFC with side-by-side streaming in a Y-shape channel, (b) cross section of
channel showing depletion boundary layers over anode and cathode and the interdiffusion zone at the liquid-liquid interface with flow-over planar electrodes on the side walls, (c) design of adding fresh reactant through multiple inlets, and (d) design of the cross-flow three dimensional flow-through electrodes.

**Figure 2:** Schematic of the fabricated fuel cell architecture with planar flow-over anode; (a) cross-sectional view; (b) exploded view, not to scale.

**Figure 3:** Schematic of the fabricated fuel cell architecture with flow-through anode; (a) cross-sectional view; (b) exploded view, not to scale.

**Figure 4:** A view of the fabricated fuel cells. Fuel inlet is on the other side of the cell, not shown in this view.

**Figure 5:** Maximum power density vs. running flow rate for planar and flow-through (FT) design with 1 M formic acid.

**Figure 6:** Planar design running on 1 M formic acid: (a) potential versus current density and (b) Power density versus current density.

**Figure 7:** Flow-through design running on 1 M formic acid: (a) Potential versus current density and (b) Power density versus current density.

**Figure 8:** Planar design running on 0.5 M formic acid: (a) potential versus current density and (b) power density versus current density.

**Figure 9:** Flow-through design running on 0.5 M formic acid: (a) potential versus current density and (b) power density versus current density.

**Figure 10:** Performance comparison of 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.

**Figure 11:** Long term performance comparison of two designs running on 0.5 and 1 M formic acid and flow rate of 100 µl/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.
Figure 1: Membraneless Laminar Flow-Based Fuel Cell, (a) Schematic sketch of membraneless LFFC with side-by-side streaming in a Y-shape channel, (b) cross section of channel showing depletion boundary layers over anode and cathode and the interdiffusion zone at the liquid-liquid interface with flow-over planar electrodes on the side walls, (c) design of adding fresh reactant through multiple inlets, and (d) design of the cross-flow three dimensional flow-through electrodes.
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Figure 11: Long term performance comparison of two designs running on 0.5 and 1 M formic acid and flow rate of 100 µl/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.