FUEL UTILIZATION IN AIR-BREATHING MEMBRANELESS LAMINAR FLOW-BASED FUEL CELL

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Abstract: This article describes the fuel utilization in air-breathing membraneless laminar flow-based fuel cells (LFFC) with flow-through (FT) and planar anodes. Because of the improved mass transport to catalytic active sites, the flow-through anode enables improved fuel utilization per single pass compared to flow-over planar anode. To draw direct conclusions for performance and fuel utilization developments, fuel cells with flow-over and flow-through anodes made of carbon-fiber-based paper were fabricated from the same materials. Experimental results from linear potential sweep voltammetry demonstrated improved power density of 26.5 mW/cm^2 for the fuel cell with flow-through anode rather than 19.4 mW/cm^2 with flow-over anode, both running on 1 M formic acid. In addition, chronoamperommetry experiment with fuel concentrations of 0.5 M and 1 M and flow rate of 100 µl/min revealed that flow-through design had higher average current density of 34.2 mA/cm^2 and 52.3 mA/cm^2 with average fuel utilization of 16.32% and 21.35 % while the planar design had the corresponding values of 25.1 mA/cm^2 and 35.45 mA/cm^2 with fuel utilization of 11.07% and 15.67%.

Keywords: Fuel cell, Membraneless fuel cell, laminar flow, Microfluidic fuel cell, fuel utilization, flow-through.

INTRODUCTION

Micro fuel cell (MFC) technology can take advantage of fuels with energy density of an order of magnitude higher than the energy stored in batteries [1]. To harvest the high energy density of fuels, the miniaturization and integration of fuel cell systems are inevitable. Membraneless laminar flow-based fuel cell (LFFC) is an attempt that aims to simplify the design and fabrication of micro fuel cells (MFCs).

As shown in Figure 1, LFFCs take advantage of the lamination of streams including fuel and oxidant reactants with an aqueous supporting electrolyte in a microchannel. Fuel and oxidant streams are introduced from separated inlets. Because of the laminar nature of the streams, a liquid-liquid interface is formed through the channel. Charge transport between the electrodes occurs inside the channel and through the co-laminar liquid-liquid interface [2].

LFFCs with air-breathing cathode avoid the need for an external oxidant reservoir. The fuel cell can take advantage of the high concentration of oxygen in air of 10 mM and the higher diffusion coefficient of oxygen in air of 0.2 cm^2 s^{-1} as compared to the respective values in aqueous media of 2–4 mM and 2×10^{-5} cm^2 s^{-1}[3]. 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 [4].

One of the major concerns of LFFCs for practical applications is low fuel utilization per single pass,
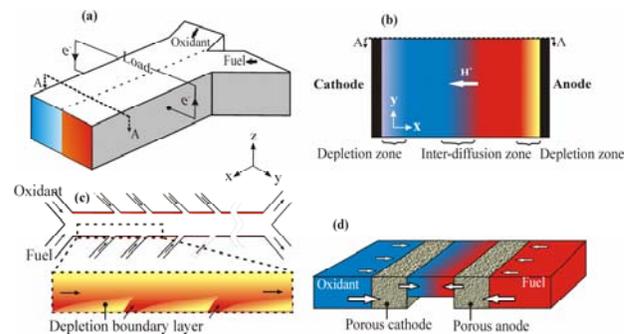

Figure 1: Membraneless Laminar Flow-Based Fuel Cell (a) Schematic sketch of membraneless LFFC with side-by-side streaming in a Y-shape channel, (b) cross section of channel showing depletion boundary layers over anode and cathode and the interdiffusion zone at the liquid-liquid interface with flow-over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

which decreases the total energy density of the fuel cell system or impose the implementation of a recirculation system. In our last investigation we proposed the concept of flow-through anode for air-breathing LFFC [5]. In this study, effect of flow-through anode architecture on fuel utilization was investigated in more details.

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. Potential sweep voltammetry and chromoamperommerty experiments were run on two fuel solutions of 0.5 and 1 M formic acid with 0.5 M sulfuric acid as supporting electrolyte.

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%. The anode contains a catalyst layer made of palladium black (Pd) with a loading of 7-8 mg/cm^2.

As shown in figure 2 The main flow channel was made of poly(methyl methacrylate) (PMMA) with a thickness of 1.5 mm from Margacipta®. 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. 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 cm^2 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.
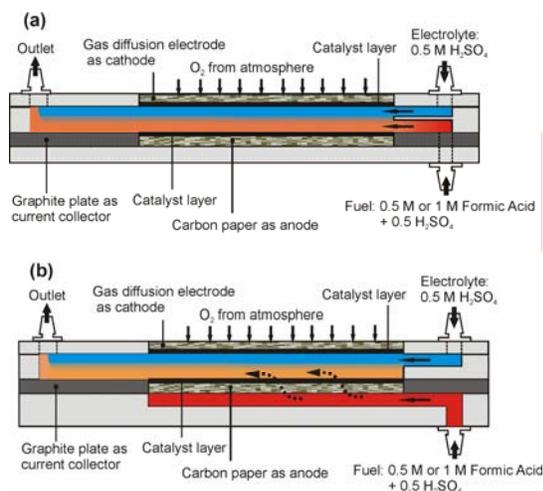

Figure 2: Schematic of the fabricated fuel cell (a) with planar flow-over anode architecture; (b) with flow-through anode architecture.

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) dehyrogenation pathway which the direct and favorite path for generating active species of 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 as follows:

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^- \qquad E^o = -0.22 \text{ V}$$
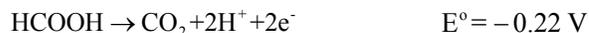
Palladium (Pd) has the tendency to break the O-H bonds of formic acid over the whole potential region. Protons travel across the channel by diffusive transport due to a gradient in proton concentration between the anode and the cathode, and by electromigration due to the voltage gradient between the electrodes [2]. Oxygen is supplied through the gas-diffusion cathode from the atmosphere. Without considering different reaction intermediates, oxygen reduction reaction (ORR) is occurred as:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^o = 1.229 \text{ V}$$

As shown in Figure 2, 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.

RESULTS AND DISCUSSIONS

The typical current-potential curves at different flow rates for planar and flow-through designs are shown in Figure 3 and Figure 4.
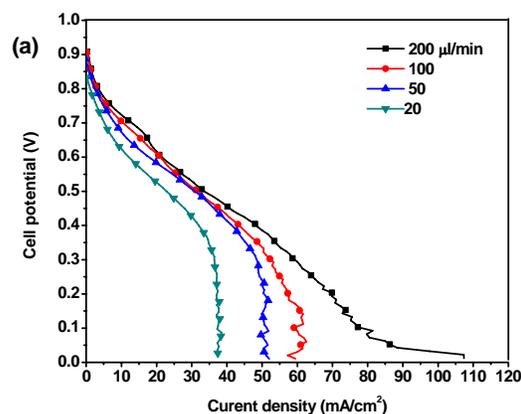

Figure 3: Potential versus current density for planar flow-over design running on 1 M formic acid.

At a flow rate of 200 µl/min, flow-over design has a maximum power density and current density (limiting 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 planar design for flow rates of 200, 100, 50 and 20 µl/min are 19.4±4.34, 17.9±5.34, 16±3.34 and 12.5±3.54 mW/cm^2 compared to 26.5±4.2, 23±4.25, 16.1±1.84 and11.4±1.19 mW/cm^2 for flow-through design.
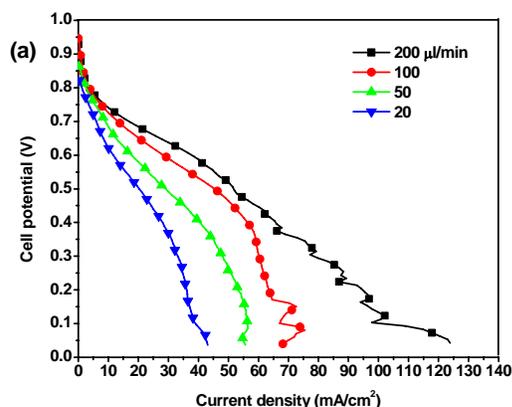
Figure 4: Potential versus current density for flow-through design running on 1 M formic acid.
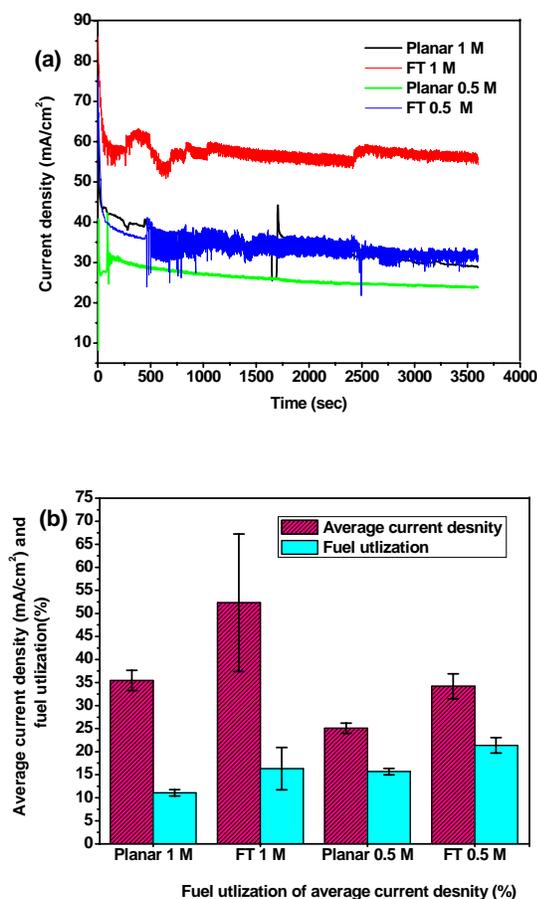

Figure 5: Long term performance comparison of two designs running on 0.5 and 1 M formic acid (a) chronoamperommetry experiment at cell potential of 0.2 V, (b) average current density and fuel utilization from the chronoamperommetry experiment for two designs.

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. To distinguish more

details of the effect of flow architecture on the cell performance, long term performance test (chronoamperommetry experiment) was carried out. 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.

As show in Figure 5, operating at two fuel concentrations of 0.5 M and 1 M, flow-through design has a higher average current density of 34.2 mA/cm^2 and 52.3 mA/cm^2 and an average fuel utilization of 16.3% and 21.4 % as compared to the planar design with corresponding values of 25.1 mA/cm^2 and 35.5 mA/cm^2 with fuel utilization of 11.1% and 15.7%. The improved cell current indicates that flow-through anode can exploit more amount of fuel for electro oxidation reaction. Since, the 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.

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