

MEMBRANELESS FUEL CELL BASED ON LAMINAR FLOW

Eric R. Choban, Piotr Waszczuk, Larry J. Markoski, Andrzej Wieckowski, and Paul J.A. Kenis*

Departments of Chemical & Biomolecular Engineering and Chemistry
University of Illinois at Urbana-Champaign
600 S. Mathews Ave.-C3, Urbana, IL 61801
kenis@uiuc.edu

ABSTRACT

An increasing societal demand for a wide range of small, often portable devices that can operate for an extended period of time without recharging has resulted in a surge of research in micropower sources. Most efforts in this area focus on downscaling of existing fuel cell technology such as the well-known proton exchange membrane (PEM) fuel cells. Here we study a novel concept for fuel cells: the use of laminar flow instead of a physical barrier such as a PEM to separate the fuel and oxidant streams. Laminar flow, i.e. low Reynolds number flow, is a property of fluid flow at the microscale: one or more liquid streams that are brought together under low Reynolds number conditions flow in parallel and contact with each other without turbulent mixing. Mass transport transverse to the direction of flow takes place by diffusion only. In our laminar flow-based fuel cell a fuel-containing stream and an oxidant-containing stream are brought together in laminar flow conditions with the electrodes placed on opposite walls within the channel. In un-optimized fuel cell configurations, current densities as high as 10 mA/cm^2 are obtained at room temperature using different fuels such as methanol or formic acid vs. oxygen saturated solvents or other oxidants.

INTRODUCTION

An increasing societal demand for a wide range of small, often portable devices that can operate for an extended period of time without recharging has resulted in a surge of research in micropower sources. These portable applications include common appliances such as cell phones, laptop computers, personal organizers, but also more specialized devices such as clinical and diagnostic tests, microanalytical systems for field tests, and global positioning systems. To date, microscale systems research has focused mostly on miniaturization of functional components, leaving miniaturization of power sources as one of the major challenges. Therefore, the exploration of micro fuel cell power sources for various microscale applications has gained significant momentum.

Current efforts in developing micro fuel cells have focused mostly on PEM-based designs, often methanol as the fuel. [Kelley, 2002; Heinzl, 2002; Sim, 2001; Jansen, 2000; Mench, 2001; Maynard, 2002] These PEM-type fuel

cell designs have great promise to become the power source of choice for some of the applications mentioned above. Yet, several technological challenges, many associated with the polymer electrolyte membrane, have prevented wide scale introduction of these fuel cells into society. [Carrette, 2000; Wasmus, 1999] Some of these technological issues include fuel crossover and membrane dry out. Most of these fuel cell systems employ methanol as the fuel. Recently formic acid is being considered because of good kinetics at ambient temperature and less dependence of the performance on the concentration of the fuel in water. [Lu, 1999; Rice, 2002]

This paper presents the use of laminar flow to obtain a membraneless fuel cell. The utilization of laminar flow with multiple liquid streams that contain different chemistries for the purpose of in-channel microfabrication and patterning has already been reported. [Kenis, 1999] This concept has led us to the development of a laminar flow-based fuel cell. [Choban, 2002] In related work, Whitesides *et al.* have shown the application of this concept in redox flow cells. [Ferrigno, 2002] A liquid/liquid interface formed by two streams is used in the laminar flow-based fuel cell studied here to keep the two fuel streams of a fuel cell localized in the cathodic and anodic areas, respectively (Figure 1). When necessary, sulfuric acid is added to the liquid streams to serve as an electrolyte. During operation, convective transport dominates over diffusive transport, resulting in direct prevention of fuel crossover by control of

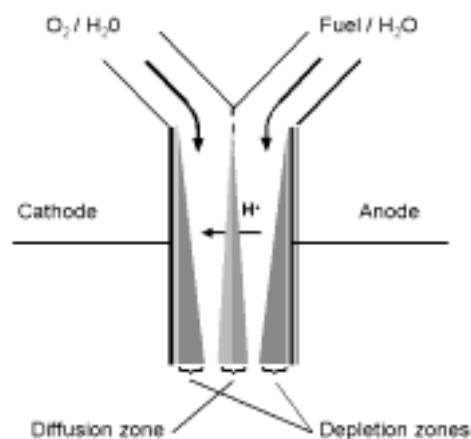


Figure 1. Schematic of the membraneless laminar flow-based fuel cell concept studied in this paper. The regions of fuel/oxidant depletion as well as the regions of diffusional fuel crossover are indicated.

flow rate. Another physiochemical phenomenon occurring is the formation of depletion boundary layers close to the catalyst-covered electrodes as a result of the reaction of fuel at the anode and oxidant at the cathode. Narrowing that depletion zone greatly enhances the performance characteristics of the fuel cell. Both depletion and diffusion zones are illustrated in Figure 1. Adjustment of the flow rates, channel dimensions, and geometries allows for the precise control of the different processes that take place at the electrodes. The liquid/liquid interface of the two streams in the laminar flow-based fuel cell discussed here has certain advantages over static membranes such as a PEM. Issues with membrane dry-out are nonexistent since there is no physical membrane. Also, the lack of a static membrane reduces the complexity of system assembly as well as cost. In this paper we will focus on the performance of the novel concept of a laminar flow-based fuel cell using different catalysts and fuels.

FUEL CELL DESIGN and FABRICATION

A Y-shaped channel structure was obtained via multiple replication steps. In a typical procedure, a negative of the channel shape, or master, is obtained in thick photoresist (SU-8 series, Microchem) via standard photolithographic techniques using transparency films as the mask. Next, this master is replicated into an elastomeric mold, typically in PDMS, to obtain a positive relief structure of the microfluidic channels. [Duffy, 1998] Then this mold is replicated to obtain the desired central support structure: for example, a liquid UV-curable adhesive (Norland Optical Adhesive) is applied and spread evenly over the elastomeric mold, then a flat layer of the elastomeric material is applied and clamped on top (i) to level the liquid adhesive, and (ii) to ensure that the top layer touches the top of the positive relief microfluidic channel structure. This clamped assembly is then treated with UV light to cure the liquid adhesive layer. Subsequently, the elastomeric top layer and the positive-relief elastomeric mold are peeled away to yield a freestanding central support structure (0.5-3 mm in thickness) carrying the outlines (sidewalls) of the Y-shaped microfluidic channel system.

Shadow evaporation of metals was used to apply the seed layers for the anodic and cathodic electrodes and leads in the appropriate shapes. Typically chromium (Cr, 2-50 nm) was applied as an adhesion layer, followed by gold (Au, 50-1500 nm) as the seed layer. Deposition of catalyst on these seed layers was performed following two procedures. In our earlier prototypes platinum black catalyst was applied via contact electrodeposition.[Choban 2002] Later, to further increase the surface area of the catalyst, nanoparticle based catalyst materials were used. These were deposited by drying catalyst containing inks on the

conductive surfaces.[Waszczuk, 2001] Catalyst loadings were typically 2.5 gr/cm^2 . Similar procedures can be used to apply different metals or combinations of different metals to the electrodes in consecutive order to tailor the catalyst on the anode and cathode, respectively, to the intended fuel and oxidant for fuel cell operation. After applying the appropriate catalyst to the cathode and anode, the central support structure is clamped between two slabs of materials, typically 1-10 mm in thickness. These slabs form the top and the bottom wall of the Y-shaped microfluidic channel embedded in the central support structure. In the experiments presented here slabs of a silicone elastomer (PDMS) were used. Glass, Plexiglas, other gasket materials (rubber, etc.), or a combination of any of such materials could be used as well.[Choban, 2002]

To guide the fuel and oxidant into the Y-shaped channel systems and to guide the waste stream out of the channel, fluidic tubing (for example PE tubing, Intramedic) needs to be placed in one of the two slabs of material. Typically holes are punched exactly at the three ends of the Y-shaped channel design. If the material is elastomeric (i.e. PDMS) the tubes can be kept in place by a pressure-fit mechanism if the diameter of the holes fits exactly the outer diameter of the tubing used. Fluid flow in all of our fuel cell experiments is regulated using a syringe pump (Harvard Apparatus) and is thus pressure driven. To provide rigidity and robustness to the layered system, more rigid top and bottom capping layers are applied, such as 2 mm-thick Plexiglas. [Choban, 2002] For the prototypes whose experiments are described in Figures 2, 3, and 4, the five layer assembly is kept together using clamps such as standard paper binding clips.

RESULTS AND DISCUSSION

Figure 2 shows a typical load curve of our laminar flow fuel cell. These curves consist of a forward and a backward potential sweep and are obtained using data acquisition equipment from National Instruments and a user interface created with Labview. In this particular example we used a 1.0 molar formic acid as the fuel and an oxygen-saturated 0.5 molar solution of sulfuric acid as the oxidant. These streams flow over electrodes covered with electrodeposited platinum black catalyst at a rate of 0.5 ml/min (i.e. $Re \approx 1$).

By using cyclic voltammetry the effective surface roughness, which is the actual surface area divided by the geometric surface area, was found to be ~ 100 . Current densities based upon this procedure are expected to be relatively low due to room temperature operation, non-optimized catalysis, and relatively low surface roughness. Deactivation of the catalyst surface is expected (and observed in the initial stages of the first experiment) due to

the adsorption of the carbon monoxide intermediate formed in the dehydrogenation of formic acid. The load curve has the typical fuel cell shape with a substantial mass transport limited area.

Figure 3 shows the performance of a laminar flow-based fuel cell that has 8 nm platinum nanoparticles as the catalyst on both the anode and the cathode. A surface roughness of around 500 was determined for this cathode and anode. This is around five times the effective roughness for electrodeposited platinum black electrodes used for the experiments in Figure 2 above. The same fuel and oxidant combination is used for the experiments shown in Figure 2.

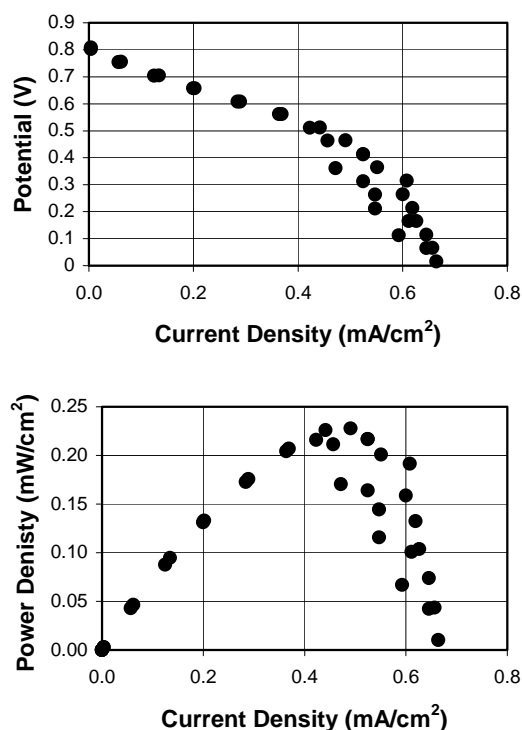


Figure 2. Load and power density curves of a laminar flow fuel cell that has electrodeposited platinum black as the catalyst on the anode and cathode. The fuel is 1.0 M formic acid and the oxidant is oxygen saturated 0.5 M sulfuric acid solution.

As expected the current density of the fuel cell using the high surface area nanoparticles instead of electrodeposited platinum is an order of magnitude higher. However, carbon monoxide poisoning of the platinum catalyst still occurs as expected. Formic acid has been shown to be a promising fuel due to the faster dehydrogenation kinetics than methanol.[Weber, 1996] A bi-metallic catalyst such as a platinum/palladium mixture

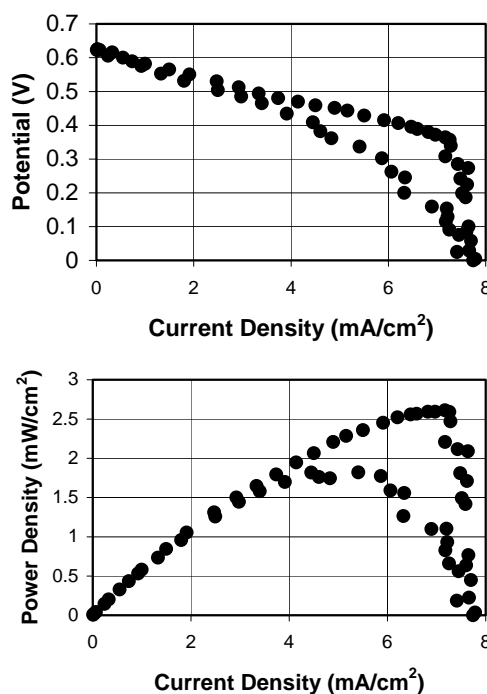


Figure 3. Load and power density curves (room temperature) of a laminar flow-based fuel cell that has platinum nanoparticles as the catalyst on both the anode and cathode. The fuel is 1.0 M formic acid in water and the oxidant is saturated 0.5 M sulfuric acid solution.

has also been shown to enhance performance.[Lu 1999, Waszczuk 2002, Rice 2002]

While formic acid seems to be a promising fuel for microfluidic fuel cells, few publications regarding its use in fuel cells have appeared to date. In order to compare our novel fuel cell concept with PEM-type fuel cell technology, we also tested our fuel cell using methanol. Due to the extreme effects of carbon monoxide poisoning during methanol oxidation on platinum, a well-established bi-metallic catalyst of platinum-ruthenium, which has been shown to reduce the amount of carbon monoxide poisoning, was used.[Waszczuk, 2001] Unsupported platinum-ruthenium nanoparticles (50/50 atomic %) were applied to the anode while platinum nanoparticles were applied to the cathode. The performance of such a laminar flow fuel cell using methanol as the fuel is shown in Figure 4. Here the performance is comparable to formic acid on the platinum nanoparticles. The methanol laminar flow fuel cell performance at room temperature is on the same order of magnitude, tens of mA/cm², of other conventional room temperature fuel cells.[Kelley, 2002] However, the most encouraging result is that the formic acid performance on non-optimized bi-metallic catalyst is similar to the methanol performance on the optimized platinum/ruthenium catalyst. Thus there appears to be significant promise for the use of

formic acid as a fuel with an optimized platinum/palladium catalyst for room temperature fuel cell operation.

The results presented above show that a laminar-based fuel cell system is feasible. One of the major advantages of this design is the direct control over fuel crossover. By designing the cell correctly, operation will occur without any fuel crossing over to the cathode. There are some limitations to the current laminar flow fuel cell design, most notably the low oxygen solubility in water. Using solvents that have a higher affinity for oxygen solubility may overcome this issue. The formation of concentration boundary layers on the anode and the cathode as fuel and oxidant are consumed is another limiting physiochemical phenomenon. This issue can be overcome by, for example, miniaturization of the fuel cell to the extent that the boundary layer can be compressed closer to the electrode, which will increase the flux of fuel and oxidant to the electrode surfaces.

As for most direct liquid fuel cell systems, liquid pumping is needed to operate the system, which will result in parasitic losses unless natural forces such as gravity or capillary forces are used. Recirculation may also be needed to operate efficiently enough to compete with current fuel cell designs. These are design issues that will be explored with further research.

CONCLUSIONS

The preliminary performance data with methanol as the fuel in a laminar flow-based microfuel cell are already not too different from the performance of conventional PEM-based fuel cells operating at room temperature. Using formic acid instead of methanol as the fuel is expected to lead to better performance in particular at ambient temperatures due to more favorable kinetics.

Multiple changes in the design and fuel/catalyst formulations are being explored to overcome some of the limitations and thus to further increase the performance characteristics of these conceptually novel microfuel cells. Currently the limiting factor in performance is the low oxygen solubility in an aqueous solvent, which can be solved by using high oxygen solubility aqueous solvents. Whether this type of membrane-less fuel cell as a system will be superior over existing PEM-based microfuel cell technology is a completely different question, and will be the topic of further investigation.

REFERENCES

Carrette L., Friedrich K. A., Stimming U., 2000, Fuel Cells: Principles, Types, Fuels, and Applications, *Chem. Phys. Chem.*, Vol. 1, pp. 162-193.

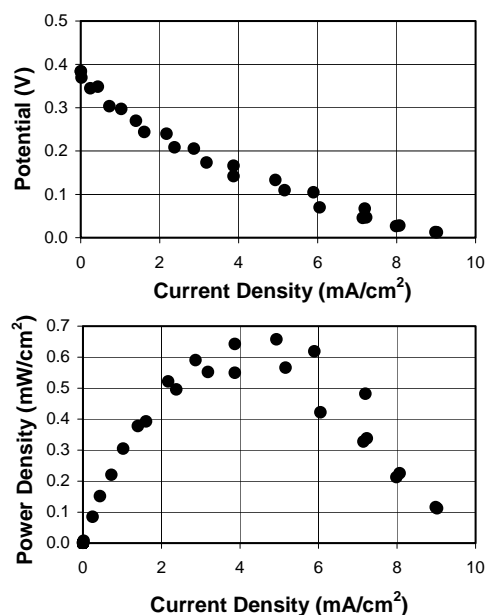


Figure 4. Load and power density curves (room temperature) of a laminar flow fuel cell that has platinum nanoparticles as the catalyst on the cathode and 50:50 platinum/ruthenium nanoparticles on the anode. The fuel is 1.0 M methanol and the oxidant is oxygen saturated 0.5 M sulfuric acid.

Chohan E. R., Markoski L. J., Stoltzfus J., Moore J. S., Kenis P. J. A., 2002, Microfluidic Fuel Cells that Lack a PEM, *Power Sources Proc.*, Vol. 40, pp. 317-320.

Duffy D. C., McDonald J. C., Schueller O. J. A., Whitesides G. M., 1998, Rapid Prototyping of Microfluidic Systems in Poly (dimethylsiloxane), *Anal. Chem.*, Vol. 70, pp. 4974-4984.

Ferrigno R., Stroock A. D., Clark T. D., Mayer M., Whitesides G. M., 2002, Membraneless Vanadium Redox Fuel Cell Using Laminar Flow, *J. Am. Chem. Soc.*, Vol. 124, pp. 12930-12931.

Heinzel A., Herbling, C., Muller M., Zedda M., Muller C., 2002, Fuel Cells for Low Power Applications, *J. Power Sources*, Vol. 105, pp. 250-255.

Jansen A., Leeuwen S. van, and Stevels A., 2000, Design of a Fuel Cell Powered Radio, a Feasibility Study into Alternative Power Sources for Portable Products, *IEEE Intl. Sym. Elec. Environ.*, pp. 155-160.

Kelley S. C., Deluga G. A., and Smyrl W. H., 2000, A Miniature Methanol/Air Polymer Electrolyte Fuel Cell, *Electrochem. Solid-State Lett.*, Vol. 3, pp. 407-409.

Kelley S. C., Deluga G. A., and Smyrl W. H., 2002, Miniature Fuel Cells Fabricated on Silicon Substrates, *AlChE J.*, Vol. 48, pp. 1071-1082.

Kenis P. J. A., Ismagilov R. F., Whitesides G. M., 1999, Microfabrication Inside Capillaries Using Multiphase Laminar Flow Patterning, *Science*, Vol. 285, pp. 83-85.

Lu G.-Q., Crown A., Wieckowski A., 1999, Formic Acid Decomposition on Polycrystalline Platinum and Palladized Platinum Electrodes, *J. Phys. Chem.*, Vol. 103, pp. 9700-9711.

Lu G.-Q., Chrzanowski W., Wieckowski A., 2000, Catalytic Methanol Decomposition Pathways on a Platinum Electrode, *J. Phys. Chem. B*, Vol. 104, pp. 5566-5572.

Maynard H. L., and Meyers J. P., 2002, Miniature Fuel Cells for Portable Power: Design Considerations and Challenges, *J. Vac. Sci. Technol. B*, Vol. 20, pp. 1287-1297.

Mench M. M., Wang Z. H., Bhatia K., and Yang C. Y., 2001, Design of a Micro Direct Methanol Fuel Cell, 2001 *Proc. ASME Intl. Mech. Eng. Cong. Expo.*, pp. 317-324.

Rice C., Ha S., Waszczuk P., Wieckowski A., Barnard T., 2002, Direct Formic Acid Fuel Cells, *Journal of Power Sources*, Vol. 111, pp. 83-89.

Sim W. Y., Kim G. Y., Yang S. S., 2001, Fabrication of Micro Power Source (MPS) Using a Micro Direct Methanol Fuel Cell for the Medical Application, *IEEE Intl. Conf. on MEMS, Tech. Digest*, 14th, pp. 341-344.

Wasmus S, Kuver A., 1999, Methanol Oxidation and Direct Methanol Fuel Cells: A Selective Review, *J. Electroanal. Chem.*, Vol. 461, pp. 14-31.

Waszczuk P., Solla-Gullon J., Kim H.-S., Tong Y. Y., Montiel V., Aldaz A., Wieckowski A., 2001, Methanol Electrooxidation on Platinum/Ruthenium Nanoparticle Catalysts, *Journal of Catalysis*, Vol. 203, pp 1-6.

Waszczuk, P., Barnard, T. M., Rice, C., Masel, R. I., Wieckowski, A., 2002, A nanoparticle catalyst with superior activity for electrooxidation of formic acid, *Electrochemistry Communications*, Vol. 4, pp. 599-603.

Weber M., Wang J.-T., Wasmus S., Savinell R. F., 1996, Formic Acid Oxidation in a Polymer Electrolyte Fuel Cell, *J. Electrochem. Soc.*, Vol. 143, pp. 158-160.