Membraneless laminar flow-based micro fuel cells operating in alkaline, acidic, and acidic/alkaline media

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Abstract

The lack of a polymer electrolyte membrane (PEM, e.g. Nafion) in membraneless, laminar flow-based micro fuel cells (LF-FCs) eliminates several PEM-related issues such as fuel crossover, cathode flooding, and anode dry-out, as we reported previously. This paper explores the media flexibility of LF-FCs by working in acidic and alkaline media, as well under “mixed-media” conditions in which the anode is in acidic media while the cathode is in alkali, or vice versa. Operating a fuel cell under alkaline conditions has positive effects on the reaction kinetics, both at the anode and cathode, while the cell performance under “mixed-media” conditions offers an opportunity to increase the maximum achievable open cell potential (OCP). The lack of media-related constraints and the simplicity of the LF-FC design allow for these experiments to be performed consecutively in a single LF-FC without changing the system, except for altering the composition/pH of the fuel and oxidant streams. The performance of LF-FCs operated with different media is described and compared.

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1. Introduction

Advances in microelectronics, microfabrication, and manufacturing continue to lead to an ever-wider variety of ever-smaller portable microelectronic systems, such as cellular phones, laptop computers, personal organizers, entertainment devices, global positioning systems and a wide range of microanalytical systems. Their performance and lifetime operation are usually limited by their respective power source, typically a rechargeable Li-ion battery. The development of long lifetime power sources for these applications is lagging behind. Micro fuel cells have the promise of addressing this issue for some of these microelectronic applications due to their greater specific energy [1,2]. In addition, fuel cells are environment-friendly and can be recharged instantly. Designing and building micro fuel cells, however, cannot be implemented by the straightforward scaling-down of established macroscopic fuel cell technologies. New chemical and mechanical engineering problems arise and need to be understood before the successful development of these microsystems can be attained [2].

Of the different types of fuel cell systems, the polymer electrolyte membrane fuel cell (PEM-FC) has been recognized as one of the most promising candidates to overcome the challenges of miniaturization [3]. The majority of the reported PEM-based micro fuel cells are fabricated using silicon microfabrication procedures adapted from microelectromechanical system (MEMS) and advanced integrated circuit (IC) technologies [1,4–7]. The precise repetitive steps of silicon etching and deposition processes enable the fabrication of microchannel structures in silicon for fuel delivery to the anode, while air is typically provided to the open cathode side of the membrane electrode assembly. Hydrogen is one of the fuels of choice for PEM-FCs, especially for macroscale systems. In order to obtain lightweight micro fuel cells with
Operation of fuel cells in alkaline media has certain advantages. When using methanol as the fuel and oxygen as the oxidant in an alkaline electrolyte: (i) the electro-oxidation of the catalyst-poisoning carbon monoxide species is improved on the anode [27] and (ii) the kinetics of the oxygen reduction reaction (ORR) at the cathode is increased [28–30]. For this reason the development of alkalimpatible electrolyte or anion exchange membranes for alkalimpatible FCs is being pursued [31–34]. However, limited long-term stability due to the potential of carbonate formation resulting in clogging of the membrane restricts the use of these alkalimpatible membranes for direct liquid fuel cell operation.

All the aforementioned membrane-related issues can be avoided in the membraneless LF-FCs studied here. The flexibility of LF-FCs in the choice of media and the performance implications of operating LF-FCs under acidic, alkaline, or even “mixed-media”, i.e., one electrode acidic and one alkaline conditions will be the focus of this study. In addition, we will discuss the advantages of being able to tailor and optimize the anode and cathode catalyst activity and stability independently in an LF-FC without restrictions due to the choice of a common media.
2. Experimental

2.1. LF-FC fabrication

Graphite plates (EDM Supplies Inc., paco grade EDM-3, 0.0001 in. particle size) serve three functions in the laminar flow-based micro fuel cells studied here (Fig. 1): (1) current collector; (2) catalyst support structure; and (3) edificial element. These graphite plates are placed side by side with a specific spacing, typically between 0.5 and 1.0 mm, and form the length of the channel where the fuel and oxidant streams flow next to each other. The inlets to this channel are milled out of the graphite plates with a drill bit at desired dimensions, typically 0.250 mm. Before assembling the fuel cell, catalyst is applied to the graphite plates (see below). The capping layers of the design are 1 mm thick polycarbonate slabs, while thin films of polydimethylsiloxane (PDMS, Dow Corning) were used as a gasket material between the polycarbonate and the graphite.

2.2. Catalyst deposition

For all experiments described in this paper, catalyst suspensions for both anode and cathode were prepared at a concentration of 4.0 mg/ml catalyst in a 10 wt. % (with respect to the amount of catalyst) Nafion solution (Nafion stock solution: DuPont, 5% (w/w) solution), and then a specific volume of the suspension was applied to those side faces of the graphite plates that line the microfluidic channel. Then solvent was evaporated by the use of a heat lamp, thus letting the catalyst adhere to the side face of the respective graphite plates at the desired loading. For the experiments described in this paper, the catalyst on the anode is unsupported Pt/Ru 50:50 at.% alloy nanoparticles (Alfa Aesar, stock 41171, lot K28K14) in 10 wt. % Nafion solution at a loading of 2 mg/cm². The catalyst on the cathode electrode is unsupported Pt black nanoparticles (Alpha Aesar) in 10 wt. % Nafion solution at a loading of 2 mg/cm².

2.3. Chemicals

Methanol (Fisher Scientific) in varying concentrations in 18.3 MΩ-cm Millipore water was used as the fuel, and oxygen (S. J. Smith Welding Supply 99.99%) dissolved in 1N sulfuric acid (Fisher Scientific) or 1N potassium hydroxide (Fisher Scientific) in 18.3 MΩ-cm Millipore water as the oxidant. In order to saturate the oxidant solution with oxygen, oxygen was bubbled through the 1N acid or the 1N alkaline solution for 15 min with a glass tube ending in a glass frit.

2.4. Fuel cell testing

Polyethylene tubing (Intramedic PE 205, i.d. 1.57 mm) is used to guide the fuel and oxidant into the LF-FC and to guide the waste stream out of the cell. Fluid flow in all the fuel cell experiments is pressure driven and regulated using a syringe pump (Harvard Apparatus PHD 2000). The operating conditions for all data and experiments reported are: flow rate per inlet channel = 0.3 ml/min; channel length = 2.9 cm; channel height = 1 mm and channel width = 0.75 mm. This flow rate and these cell dimensions correspond to a Reynolds number of around 0.1, which is well within the laminar flow range. In order to analyze the individual performance of each electrode, an external Ag/AgCl reference electrode in a 3.0 M NaCl solution (BAS, West Lafayette, IN) was placed in a small compartment filled with 1N sulfuric acid and connected to the laminar flow-based fuel cell using capillary tubing (i.d. 1.57 mm) ending in the waste stream collection beaker. A detailed description of LF-FC analyses with this external reference electrode configuration can be found elsewhere [35]. Polarization curves were obtained using an in-house fabricated fuel cell testing station equipped with a data acquisition device (FP-1000 with FP-AI-100 and FP-TB-10 modules, from National Instruments, Austin, TX), and a user interface created with Labview (National Instruments, Austin, TX). During the experiment, the potential steps were controlled manually, and the current was recorded after reaching a steady state value.

3. Results and discussion

3.1. Laminar flow-based fuel cells

In the LF-FC configuration used in this study the graphite plates serve the three purposes of catalyst support—structure, current collector, and edificial element (Fig. 1). Unsupported catalytic Pt/Ru alloy nanoparticles (anode) and unsupported Pt nanoparticles (cathode) are applied to the sides of the graphite plates that line the microfluidic channel. Using cyclic voltammetry, we determined a resultant surface roughness factor of approximately 500 for both nanoparticle-based catalysts used. A gasket material, for example, polydimethylsiloxane, seals the top and bottom of the microfluidic channel. This three-layer assembly is clamped between two rigid polycarbonate support structures to obtain an LF-FC test cell that can be easily inspected visually. Also, graphite plates can be exchanged easily if needed. When injected through the inlets, fuel and oxidant solutions will merge at the Y-junction and continue to flow laminarily in parallel over the anode and cathode where fuel and oxidant are allowed to be oxidized and reduced, respectively.

3.2. Media flexibility in LF-FCs

As mentioned above, this membraneless, all liquid design eliminates issues related to fuel crossover, anode dry-out, and cathode flooding [16,18,19]. In addition, lack of a membrane also allows for operation of LF-FCs in media other than acidic, the topic of this paper. Moreover, the chemical composition of the cathode and anode streams can be tailored individually to optimize individual electrode kinetics as...
and catholyte media composition combinations. The pH of the electrolyte has an effect on reaction kinetics at the individual electrodes, as well as the electrode potential at which oxidation or reduction occurs [27,28,36–38]. Eqs. (1)–(4) show the half-cell reactions and standard electrode potentials of methanol oxidation and oxygen reduction in acidic and in alkaline media, respectively. Eq. (5) represents the overall cell reaction, in all-acid or all-alkaline media. Both the alkaline–alkaline case and the acidic–acidic case have a maximum theoretical open circuit potential (OCP) of 1.21 V. The different OCPs of unusual mixed-media LF-FC configurations will be discussed below, in Section 3.4.

3.3. LF-FCs in all-acidic and all-alkaline media

Fig. 2a and b show the performance of an LF-FC in all-acidic and all-alkaline media, respectively. Initially at low current densities both the polarization curves of Fig. 2a and b are identical, and thus the performance of the LF-FC is independent of media. The mass transport limitation region, however, is reached much sooner at around 4 mA/cm² in the LF-FC running in alkaline media versus around 7 mA/cm² in the LF-FC running in acidic media. To more accurately determine the cause of the mass transport limited area, an external reference electrode was added to the system [35]. The use of an external reference electrode allowed for separate analysis and evaluation of individual electrode performance characteristics rather than just of the overall cell performance (sum of anode and cathode performances). Fig. 2c and d show that the process in both acidic and alkaline media is cathode-limited. This limitation can be attributed to the low oxygen concentration in solution. In acidic media the saturation concentration of oxygen is about 1 mM whereas the saturation concentration of oxygen in alkaline media is approximately 25% lower [40]. This difference in solubilities explains the earlier drop in performance in I-V curve of the LF-FC experiment run in the alkaline media (Fig. 2b) compared to that run in acidic media (Fig. 2a). Overpotentials of the individual electrodes in different media, as deduced from Fig. 2c and d, are in agreement with those reported previously [28–30]. Multiple tests with the same LF-FC were run over several days without any drop in activity or performance. No issues with carbonate formation were encountered in this LF-FC, as any carbonate that does form is immediately removed from the system by the flowing streams.

3.4. LF-FCs in mixed-media 1: acidic anode, alkaline cathode

After studying LF-FC performance while operating in all-acidic and all-alkaline media (Fig. 3), we studied

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Open circuit potentials (±3%) in an LF-FC operated at a flow rate of 0.3 ml/min/channel in the absence of fuel and oxidant for different anolyte and catholyte media composition combinations.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open circuit potentials</td>
<td>Potential (V)</td>
</tr>
<tr>
<td>Anode</td>
<td>Cathode</td>
</tr>
<tr>
<td>1.0N H2SO4</td>
<td>1.0N H2SO4</td>
</tr>
<tr>
<td>1.0N H2SO4</td>
<td>1.0N KOH</td>
</tr>
<tr>
<td>1.0N KOH</td>
<td>1.0N H2SO4</td>
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<tr>
<td>1.0N KOH</td>
<td>1.0N KOH</td>
</tr>
</tbody>
</table>

Before running actual fuel cell experiments, we determined the open circuit potentials for an LF-FC while flowing anode and cathode streams of different pH, but in the absence of fuel and oxidant (Table 1). At open circuit, both anode and cathode are slightly oxidized. The differing thermodynamics of Pt oxide formation in acid and alkali create a significant OCP, 0.70 V and −0.68 V, respectively, when the cathode is alkaline and anode acidic, and when the anode is acidic and the cathode is alkaline. The liquid–liquid junction potential (LJP) formed at the interface between the acidic and alkaline streams may reduce or increase the open circuit potential, depending on which stream is acidic and which is alkaline. The LJP may be estimated using the Henderson equation [39], yielding a maximum value of 32 mV in our experiments. Thus the LJP does not significantly contribute to the observed phenomena described below.
“mixed-media” systems in which one stream is acidic while the other stream is alkaline. Note that in mixed-media configurations the neutralization reaction of $\text{OH}^-$ and $\text{H}^+$ to water occurs at the liquid–liquid interface between the fuel and oxidant stream. This reaction is mildly exothermic, but we never observed an increase in temperature in the cell or in the outlet stream. The LF-FC cell dimensions and operation conditions used the result in residence times and diffusional mixing zone widths that are such that local heating effects on the performance can be neglected in the flowing microfluidic fuel cell studied here. Two configurations were considered: an acidic anode stream combined with an alkaline cathode stream (mixed-media 1) and an alkaline anode stream combined with an acidic cathode stream (mixed-media 2). In the first configuration, the overall cell reaction, Eq. (6), can be obtained from Eqs. (1) and (4):

Mixed-media 1: acidic anode, alkaline cathode

<table>
<thead>
<tr>
<th>Anode</th>
<th>$2\text{CH}_3\text{OH} + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>$3\text{O}_2 + 6\text{H}_2\text{O} + 12\text{e}^- \rightarrow 12\text{OH}^-$</td>
</tr>
<tr>
<td>Overall</td>
<td>$2\text{CH}_3\text{OH} + 3\text{O}_2 + 8\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{OH}^-$ + $12\text{H}^+$</td>
</tr>
</tbody>
</table>

The maximum theoretical OCP is 0.38 V in this mixed-media configuration 1. An OCP of less than 0.1 V is observed due to the overpotentials on the cathode and anode. The energy liberated in the methanol oxidation and oxygen reduction reactions is mostly consumed by the water ionization reaction. This configuration, which couples an electrolytic reaction with a galvanic reaction, is thus incapable of yielding useful amounts of energy, and was not studied any further.

3.5. LF-FCs in mixed-media 2: alkaline anode, acidic cathode

In contrast, in mixed-media configuration 2, use of an alkaline anode stream (Eq. (3)) and an acidic cathode stream (Eq. (2)) allows energy to be obtained both from the methanol oxidation/oxygen reduction reactions and from the acid/alkali electrochemical neutralization reactions, as evident from the overall cell reaction (Eq. (7)):

<table>
<thead>
<tr>
<th>Anode</th>
<th>$2\text{CH}_3\text{OH} + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>$3\text{O}_2 + 6\text{H}_2\text{O} + 12\text{e}^- \rightarrow 12\text{OH}^-$</td>
</tr>
<tr>
<td>Overall</td>
<td>$2\text{CH}_3\text{OH} + 3\text{O}_2 + 8\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{OH}^-$ + $12\text{H}^+$</td>
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$$E^0 = 0.02 \text{ V} \ [38]$$

$$E^0 = 0.40 \text{ V} \ [37]$$

$$\Delta E = 0.38 \text{ V}$$

Fig. 2. Load curves for overall cell performance of an LF-FC operating in: (a) alkaline; (b) acidic media; (c) and (d) the corresponding $I$–$V$ curves of individual electrode performances. For both experiments the fuel stream is 1.0 M methanol in 1N KOH (a, c) and in 1N H$_2$SO$_4$ (b, d) and the oxidant stream is oxygen-saturated 1N KOH (a, c) and 1N H$_2$SO$_4$ (b, d).
mixed-media 2a: alkaline anode, acidic cathode (region I, Fig. 3b)

Anode: \[2\text{CH}_3\text{OH} + 12\text{OH}^- \rightarrow 2\text{CO}_2 + 10\text{H}_2\text{O} + 12\text{e}^-\]

Cathode: \[12\text{H}^+ + 12\text{e}^- + 3\text{O}_2 \rightarrow 6\text{H}_2\text{O}\]

Overall: \[2\text{CH}_3\text{OH} + 3\text{O}_2 + 12\text{OH}^- + 12\text{H}^+ \rightarrow 2\text{CO}_2 + 16\text{H}_2\text{O}\]

The coupling of two galvanic reactions in this configuration yields a desirable high theoretical OCP of 2.04 V. However, because of the overpotentials resulting from the slow kinetics of oxygen reduction and methanol oxidation, the open circuit potential is reduced to a measured value of 1.4 V (Fig. 3a). For comparison, typical PEM-based direct methanol fuel cells (DM-FCs) typically have OCPs of 0.5–0.7 V and would be operated at a cell potential of 0.35–0.45 V (see, for example, 1). Note that sustained high potentials at usable current densities directly translate into higher power densities.

This LF-FC run in the acidic cathode/alkaline anode configuration is still limited by oxygen mass-transfer. The poor oxygen supply causes the cathode potential to drop from around 0.8 V at open circuit to about –0.2 V (both versus Ag/AgCl) at about 7 mA/cm² (region I in Fig. 3b), the same current density at which the all-acidic LF-FC reaches its cathode-limited performance regime (Fig. 2d).

At higher current densities, a unique phenomenon for fuel cells is observed. Once the potential of the cathode of the LF-FC in this mixed-media configuration reaches approximately –0.2 V versus Ag/AgCl at an unusual tail in the acidic cathode polarization curve (region II in Fig. 3b) appears. The cell potential remains almost constant at 0.35–0.45 V over the 8–40 mA/cm² current density range. This phenomenon occurs when the proton reduction (Eq. (8)) becomes an additional cathode reaction. At high current densities, proton reduction surpasses oxygen reduction (Eq. (3)) to become the predominant cathode reaction. The ability of proton reduction to occur at current densities much higher than the oxygen reduction limiting current density is due to the much larger concentration of protons, \([\text{H}^+] = 1 \text{M versus } [\text{O}_2^0] \approx 2 \text{mM, leading to the overall cell reaction of Eq. (9).}\]

Mixed-media 2b: alkaline anode, acidic cathode (region II, Fig. 3b)

Anode: \[2\text{CH}_3\text{OH} + 12\text{OH}^- \rightarrow 2\text{CO}_2 + 10\text{H}_2\text{O} + 12\text{e}^-\]

Cathode: \[12\text{H}^+ + 12\text{e}^- \rightarrow 6\text{H}_2\]

Overall: \[2\text{CH}_3\text{OH} + 12\text{OH}^- + 12\text{H}^+ \rightarrow 2\text{CO}_2 + 10\text{H}_2\text{O} + 6\text{H}_2\]

In this high current density regime of this mixed-media LF-FC (region II, Fig. 3b), the current density continues to increase at a constant cathode potential until the anode becomes the limiting factor. The anode potential slightly increases over the 8–40 mA/cm² range until a rapid increase at current densities larger than 42 mA/cm² due to the mass-transfer limitations (Fig. 3b). Such mass-transfer limited behavior is commonly observed for the methanol oxidation under these conditions [29,34].

\[E^0 = -0.81 \text{ V [38]}\]  
\[E^0 = 1.23 \text{ V [37]}\]  
\[\Delta E = 2.04 \text{ V} \]

Operating in this mixed-media configuration, with an alkaline anode and an acidic cathode, resulted in a higher overall cell potential than those obtained for the all-acidic and all-alkaline LF-FC experiments. For example, at a potential of 0.8 V, the mixed-media configuration provides a current density of 7 mA/cm², whereas both the all-acidic and all-alkaline cells already start from a lower OCP, and thus have cell potentials that are significantly lower than those of the mixed-media configuration. Moreover, a current density of 7 mA/cm² is unattainable for the all-alkaline configuration, while the all-acidic configuration has a cell potential of less than 0.35 V at this current density.

Fig. 4 shows the power density curves of the three LF-FC experiments performed in different media combinations at the anode and cathode. While the all-acidic and all-alkaline LF-FC experiments have maximum power densities of 2.4 and 2.0 mW/cm², respectively, both at a cell potential of about 0.5 V, the mixed-media experiment results first in a local power density maximum of almost 5 mW/cm² at a cell potential of about 1 V. Within this sub-10 mA/cm² regime, the mixed-media fuel cell clearly outperforms both the all-acidic and all-alkaline fuel cell. At current densities above 10 mA/cm² the mixed-media fuel cell reaches an even higher global maximum power density of 12.0 mW/cm² due to the unusual tail in the cathode potential caused by proton reduction. The higher power densities in the mixed-media LF-FC are a direct result of higher overall cell potentials due to the unprecedented ability to operate the cathode and anode at different pH in an LF-FC.

On first sight, the higher power densities of the mixed-media LF-FC configuration may look very promising. These higher power densities and higher cell potentials of the mixed-media LF-FC come, however, at a significant price. In the previously discussed all-acidic and all-alkaline configurations, the \[\text{OH}^- \text{ and } \text{H}^+ \text{ species, respectively, are reactants at both the electrodes, but there is no net generation or consumption. In any future all-alkaline or all-acidic LF-FC-based fuel cell system, these alkaline and acidic streams would be recirculated with the continuous replenishment of oxidant and fuel. In contrast, in the mixed-media LF-FC, the}

Mixed-media 2b: alkaline anode, acidic cathode (region II, Fig. 3b)

Anode: \[2\text{CH}_3\text{OH} + 12\text{OH}^- \rightarrow 2\text{CO}_2 + 10\text{H}_2\text{O} + 12\text{e}^-\]

Cathode: \[12\text{H}^+ + 12\text{e}^- \rightarrow 6\text{H}_2\]

Overall: \[2\text{CH}_3\text{OH} + 12\text{OH}^- + 12\text{H}^+ \rightarrow 2\text{CO}_2 + 10\text{H}_2\text{O} + 6\text{H}_2\]
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Fig. 3. (a) Load curve of an LF-FC with an alkaline anode and acidic cathode. For comparison, also the load curves of the LF-FCs run in all-alkaline (Al) and in all-acidic (Ac) media are included. (b) Corresponding individual electrode performance curves for the mixed-media configuration: Anode (top) and cathode (bottom). For this experiment, the fuel stream is 1.0 M methanol in 1 N KOH and the oxidant stream is an oxygen-saturated 1 N H₂SO₄ solution.

Fig. 4. Power density curves for overall cell performance of an LF-FC operating in alkaline (1 N KOH), acidic (1 N H₂SO₄), and mixed-media (anode: 1 N KOH and cathode: 1 N H₂SO₄). For all experiments the fuel stream is 1 M methanol, and the oxidant stream is an oxygen-saturated solution in the respective media.

4. Conclusion

The experiments described in this paper show that membraneless LF-FCs are media flexible; they can be operated in all-acidic, all-alkaline, or even mixed-media configurations. No changes to the fuel cell are needed when changing oxidant or fuel stream composition. In contrast to PEM-based fuel cells, the lack of a membrane in an LF-FC eliminates the issue of membrane clogging by carbonates. Any carbonates that do form are immediately removed from the system by the flowing streams. Uniquely, the LF-FC enables individual tailoring of the composition of fuel and oxidant streams, thus allowing the oxidation and reduction kinetics at the anode and cathode, respectively, to be maximized independently. The LF-FC cell can thus be run in a mixed-media configuration in which the anode can be acidic while the cathode is alkaline, or vice versa, to improve individual electrode kinetics and thermodynamics. Certain combinations of anode and cathode stream composition, however, will result in very low OCPs, while other combinations will lead to highly desired high OCPs as a result of the pH dependence of standard electrode potentials. In this work, we showed that the acidic anode/alkaline cathode mixed-media configuration leads to an approximately 0 V measured OCP, while the alkaline anode/acidic cathode mixed-media configuration leads to a very high measured OCP of 1.4 V.

The performance of LF-FCs run in all-acidic and all-alkaline conditions, like in our previous work [16,18,19], is still limited by mass-transfer and a low oxygen concentration at the cathode to maximum current densities of 10 mA/cm² and maximum power densities of 2.5 mW/cm². Better performance of the LF-FCs as a result of better electrode kinetics both for methanol oxidation and oxygen re-
duction under all-alkaline conditions could not be observed due to the dominating mass-transfer limitations at the cathode. Once the mass-transfer limitation at the cathode in the present LF-FC designs is addressed, further characterization of the all-alkaline LF-FC is needed to utilize the benefits of superior reaction kinetics in alkaline media.

For the LF-FC operated in the alkaline anode/acidic cathode mixed-media configuration, a large OCP of 1.4 V was measured, which, in light of the known overpotentials at both the cathode and the anode, is in good agreement with the theoretical OCP of 2.04 V. These large potentials result in a rather unusual phenomenon for fuel cells; at high current densities, once the oxygen has been depleted from the exodi stream, proton reduction becomes the cathode reaction. Much higher current densities, as high as 40 mA/cm², are obtained. The high current densities and a higher OCP (and thus higher potentials under load conditions) resulted in a maximum power density of 12 mW/cm². On first sight, this mixed-media LF-FC seems to outperform the all-acidic and all-alkaline LF-FCs. Most of the observed extra power density for this mixed-media LF-FC configuration is supplied, however, by the net consumption of protons on the cathode and hydroxide ions at the anode. Taking into account the consumption of H₂SO₄ and KOH a maximum theoretical energy density for this mixed-media LF-FC configuration can be calculated that is merely one-fifth of the maximum energy density of all-acidic or all-alkaline LF-FCs that consume only methanol. The mixed-media LF-FC configuration thus does not compare favorably to all-acidic or all-alkaline LF-FCs.

The media flexibility of LF-FCs allows for anode and cathode catalysts to be chosen irrespective of their individual media constraints, and thus lifts the common electrolyte restraint on fuel cell catalyst design. “Mixed-media” LF-FCs thus may hold promise for the development of micro fuel cells with unusual combinations of anode and cathode chemistries. For example, in biofuel cell applications, finding a pH at which both the anode and cathode enzymes exhibit sufficient activity and stability is often a challenge [41]. Use of an LF-FC design would allow for each enzyme to operate in a media of a pH that maximizes its individual performance and long-term stability.

Implementation of LF-FCs in fuel cell systems that can compete with state-of-the-art power systems such as rechargeable Li-ion batteries will require multiple adjustments; the fuel utilization in LF-FCs, presently less than 10%, will need to be increased, for example by recirculation of the streams as has been shown for micro flow cells for different purposes in the past. More importantly, the cathode mass-transfer/oxygen solubility limitation needs to be addressed. Increasing the oxygen saturation concentration of the oxidant stream by use of perfluorocarbon-based emulsions [42,43], or by using other electrolytes, such as certain salts, that are known to increase the oxygen saturation concentration, is a first, straightforward option [40]. Alternatively, the cathode design could be adjusted to enable the use of a gaseous oxygen or air supply, similar to the oxygen-permeable membrane based cathode reported by Nuzzo et al. [10]. Investigations to address cathode limitations as well as the development of LF-FC-based fuel cell system designs involving recirculation are in progress.

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