Microfabricated fuel cells

J.S. Wainright a, c, R.F. Savinell a, c,*, C.C. Liu a, d, M. Litt b, c

a Department of Chemical Engineering, Case Western Reserve University, Cleveland OH 44106-7217, USA
b Department of Macromolecular Science, Case Western Reserve University, Cleveland OH 44106-7217, USA
c Yeager Center for Electrochemical Sciences, Case Western Reserve University, Cleveland OH 44106-7217, USA
d Electronics Design Center, Case Western Reserve University, Cleveland OH 44106-7217, USA

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Abstract

This paper reports design, materials, and testing of microfabricated fuel cells that can be applied for small power generation. Multiple co-planar fuel cells in series have been built onto ceramic substrates (as well as silicon and polymer, but not reported here) using thick-film fabrication techniques. Testing of these fuel cells gave power densities in the milliwatt (per square centimeter) range for continuous power and tens of miliwatts under pulsing conditions, and have indicated performance limiters and opportunities for higher power densities. These fuel cells are intended to operate on ambient-supplied air, and thus the polymer electrolytes must be capable of operating under a range of humidity conditions. The target conductivity for these low power devices is $>1 \text{ mS cm}^{-1}$ at 15% RH. Although novel polymer electrolytes are being pursued at CWRU for this application, we report here Nafion® films cast from alternate solvents that have adequate conductivity for this application. Several on-board fuel storage approaches are being pursued. We have demonstrated high fuel utilization by a fuel cell operating with on-board source of hydrogen from aqueous sodium borohydride, as well from solid metal hydride systems.

Keywords: PEM; Nafion®; Micropower; Hydrogen storage; Hydride

1. Introduction

Efficient small-scale power generation is critical to realizing the full benefit of many portable electronic devices. Wireless electronic devices, e.g. micro sensors and micro electromechanical or microfluidic systems, require electrical power for operation and data transmission. The availability of on-board power with appropriate sized power and energy capabilities, coupled with wireless data transmission, will open numerous possibilities for self-sustaining devices for remote or difficult to access locations. The power and energy needs for small portable devices may vary considerably depending on their design and function. Small microfabricated fuel cells open the door for energy delivery devices with independent sizing of power and energy capacity, while having the capability to supply short pulses of peak power without significant adverse effect on energy utilization. Finally, such fuel cells have the potential for energy densities significantly greater than present and predicted battery technology.

Small fuel cells with various degrees of microfabrication have been reported in the literature. Thin film techniques were used to create flowfields [1–3], some with current collections and catalyst layers [4–8] on a silicon substrate that were attached to a free-standing Nafion® film. Morse et al. [9] did not use a free-standing film, but instead spin-cast a membrane on the microfabricated support components. Individual fuel cell sizes were from 2 to 10 mm on a side, and down to 15 µm on a side. Temperatures above room temperature during testing were maintained by an oven and fuel (hydrogen or methanol) was supplied from an external source.

This paper presents concepts and results arising from a program to develop a small and completely microfabricated polymer-based fuel cell with on-board hydrogen storage. The approach is to co-fabricate a sensor or sensor suite with sufficient analog/digital circuitry for...
signal conditioning/processing, wireless communications capability (low-power RF) and a power source on a single wafer. The anticipated power requirements are for extended periods of very low (sub-milliwatt) power draws to power the sensor, with random or periodic pulses of 10–100 of milliwatts required for signal processing or data transmission. Potential operational lifetimes are from hours to days (surveillance at a particular location) to years (machinery monitoring). Development of a microfabricated power source is an enabling technology for the autonomous sensor concept. It is envisioned that this device would operate in a passive mode, without active control of temperature, humidity, reactant pressure or flow rate. This greatly simplifies the construction and operation of the fuel cell. The power density achievable in passive operation will naturally be less than that obtained in conventional fuel cells. However, the applications envisioned do not require high power densities.

2. Design principles and fabrication issues

The CWRU microfabricated fuel cell is being developed by using the following guiding principles:

- completely passive device-no fans, pumps, compressors to move reactants
- ambient temperature operation-no cooling or heating
- hydrogen fueled at near atmospheric pressure
- no external humidification-operation at ambient relative humidity
- fabrication process compatible with silicon-based microelectronics

The basic design of the fuel cell consists of a planar array of edge collected cells, such that all of the cathodes are exposed to the ambient air, while beneath all of the anodes is a common fuel manifold. Each of the components of the cells, current collectors, gas diffusion layers, catalyst layers, and electrolyte, is deposited in turn using thick film printing techniques. The hydrogen storage/generation capability is similarly fabricated in a second substrate, and bonding the two substrates together creates the final device. A schematic of the final device is shown in Fig. 1 and a photograph is shown in Fig. 2. This fabrication process is considerably different from the conventional PEM fuel cell stack construction in which individual components (electrolyte membranes, gas diffusion layers, bipolar plates, gaskets, endplates, etc) are separately manufactured, and then assembled into the stack. The following two sections will focus on the particular fabrication issues that have been addressed for the current collectors and the polymer electrolyte.

2.1. Current collectors/gas diffusion layers

In order to minimize the number of fabrication steps, the gas diffusion layer (GDL) in the microfabricated fuel cell is also used as the current collector. Typical gas diffusion layers for conventional PEM fuel cells such as carbon cloth or carbon paper have a thickness on the order of 300 μm, porosities on the order of 80%, and conductivities on the order of 50–100 S cm⁻¹. The relatively low conductivity is sufficient given that they are used in conjunction with ribbed flow fields with feature sizes on the order of 1 mm. However, for an edge-collected device, the conductivity required is considerably greater. In addition, with the thick film process, a thickness of 10–50 μm is more realistic, while 300 μm is very difficult to achieve.

The voltage drop along the current collector is given by

\[ \Delta \varphi_{i} = (L^2/2)(i_{avg}/1\sigma) \]

where \( L \) is the length of the electrode perpendicular from the current-collector edge, \( i_{avg} \) is the average current density normal to the surface and assumed to be uniform, \( \sigma \) is the conductivity of the current collector.

Assuming that a maximum voltage drop of 10 mV over a 1-cm long current collector is desired for a fuel cell current density of 50 mA cm⁻², a 25 μm thick film needs to have a conductivity of 1000 S cm⁻¹. Since the current collector must also be highly porous in order to act as a gas diffusion layer, it is clear that carbon-based materials are not ideally suitable for this component. Instead, metallic conductors are preferred. Our experience with attempting to thick film print current collector/GDLs based on metallic conductors has been that the difficulty lies in achieving sufficient porosity. In Fig. 3, fuel cell polarization curves are shown for two cells, one having a 30 μm thick printed current collector/GDL, the other with a 50 μm thick film of the same porous material. In both cases there is an appreciable loss due to diffusion of the reactants through the current collector/GDL layer, and the loss is considerably greater with the thicker film.

Additional gas permeation resistance can be expected through the substrate that supports the current collector. In practice, the inks are not printed directly onto the substrate because the pores are too large, and the ink from printing the current collector will fill the pores, thus increasing the gas permeation resistance substantially. For the fuel cells tested here, a thin porous nylon film (MAGNA nylon, pore diameter of .45 μm, Osmonics Inc.) was secured onto a substrate and then non-porous insulating boundaries and current collectors were printed. The other fuel cell layers were then sequentially printed. The completed fuel cell with nylon
backing was then attached to a ceramic wafer with slots for gas access to the anode. The hydrogen gas then passed through the slots and the porous nylon film to reach the anode surface for oxidation. The observed limiting currents with this cell design were 10–30 mA cm$^{-2}$ with one atmosphere hydrogen gas feed.

### 2.2. Electrolyte issues

There are a number of electrolyte issues that must be considered. Like other macro PEM fuel cells, the electrolyte must be proton conducting, have a favorable environment for electrode reaction kinetics, and must permit gas access to the polymer-catalyst interface so reaction can occur. In a small microfabricated fuel cell, since the current density will be low under ambient air operation, the conductivity only needs to exceed approximately 1 mS cm$^{-1}$ (125 mV IR loss at 50 mA cm$^{-2}$ with a 25 μm film). However, this conductivity level must be achievable even at low relative humidities since gas hydration is not feasible in a small passive device. We have established as a working target a conductivity greater than 1 mS/cm over the relative humidity range of 15 < RH < 100%.

A typical 5% Nafion®–alcohol solution has too low of a viscosity to print a well-defined film. In addition it has low proton conductivity at low relative humidities as shown in Fig. 4. We modify the commercially available Nafion®–alcohol solution by adding higher boiling
solvents, then concentrating the Nafion® solute. Films were cast and the solvent was evaporated under vacuum at about 80°C. The conductivity of films cast from DMSO and ethylene glycol (EG) are shown in Fig. 4, and the Nafion®/EG film meets our conductivity goals. These films were ca. 25 μm thick and were cast from 10 to 15 wt.% solutions, with the majority of the solvent being the higher boiling component.

Another issue is to deposit electrolyte precisely where it is needed. This is necessary to achieve densely packed cells that make the most use of the available area on the substrate and minimize the length of the current collectors. In addition to minimizing current collector lengths, printing patterned electrolyte layers for each cell, as opposed to having several cells sharing a continuous film of electrolyte, eliminates any shunt currents that may otherwise occur in series connected cells.

In Fig. 5a and b are two examples of thick film printing of the modified Nafion® solution. The solution used to produce Fig. 5a is clearly superior, the electrolyte films are well-defined, and can be closely spaced. The result shown in Fig. 5b is not acceptable, the electrolyte film spreads beyond the desired area when printed, and adjacent cells must be further apart. In addition, the film thickness in Fig. 5a is ≈ 90 μm and uniform across the area of the cell, while in Fig. 5b, the film thickness varies between 5 and 15 μm. While thinner electrolyte films may be preferred to minimize resistive losses, films less than 25 μm thick can lead to excessive hydrogen crossover, particularly for air-breathing devices such as these where operating current densities are low as compared to pressurized macro-size fuel cells. The solution used to cast the film in Fig. 5a consisted of about 40 mg of Nafion® and 60 mg of EG with all the alcohol and water of the original 5% Nafion®/alcohol solution removed. The solution used to cast Fig. 5b was similar, but without all of the alcohol and water removed. It was of lower viscosity and Nafion® density. The actual properties (gel content, viscosity, etc) of the casting solution varied somewhat depending on the processing procedure.

A calculation that estimates the effect of a Nafion® 1100 membrane thickness on cross-over is given in Fig. 6. The cross-over rate is also reflected in a lowering of the open circuit potential because of the mixed electrode reaction (hydrogen oxidation coupled with oxygen reduction) at the cathode. These calculations are based on kinetic parameters taken from experimental data of typical conventional PEM fuel cells operated in our laboratories. The drop in OCV as the membrane becomes thinner will be a strong function of the actual catalyst loading. However, as shown, for a water saturated Nafion® 1100 film, the cross-over rate increases appreciably for films thinner than 25 μm.

While the Nafion®/EG system appears adequate for microfuel cell applications, it still has its limitations. For example, the conductivity at low RH, although acceptable for low current density operation, will limit pulse power capability. Also, these films will swell excessively at 100% RH and the film will delaminate from the substrate thus resulting in failure. Other electrolyte systems are under development in our laboratories, and progress on these approaches are reported elsewhere [10,11].

3. Fuel cell performance

The performance of representative microfabricated fuel cells are shown in Fig. 7. These fuel cells are all microfabricated by thick film deposition. The current collection/flowfields are 15 μm thick gold printed using an Ercon ink. The electrodes were printed from a slurry of particles of C/Pt (40 wt.% Pt on XC-72 from Etek Inc.). It was necessary to have thin electrodes (2–5 μm) to avoid mud-cracking upon drying. The catalyst loading therefore was only 0.2 mg cm⁻² for both electrodes. The Nafion® was cast from a Nafion®/EG
solution. The porous substrate was a nylon porous film. The fuel cell was operated in air at 42% RH at 24°C with humidified hydrogen. The power output at 0.5 V/cell was 2 mW cm⁻² continuous, 5 mW cm⁻² for 180–300 s durations, and 50 mW cm⁻² under a 10 ms pulse. Although long term testing was not carried out, there was no noticeable decay in performance over a 20-h period. Also shown for comparison is the polarization curve from a fuel cell fabricated by applying the inks onto a free-standing Nafion® film. The limiting current of this polarization curve is due to the diffusion of oxygen through the porous metal current collector.

The pulse capability of this fuel cell is shown in Fig. 8. In this case the air R.H. was at 48%. The duty cycle was 90% at 0.5 mA cm⁻² and 10% at a higher current. The pulse width was 10 ms. When the pulse current was 50 mA cm⁻² the voltage stayed above 0.5 V for over 600 s of cycling. After about 600 s, the voltage did not recover adequately after each pulse and consequently dropped below 0.5 V after about 600 s. The time to reach the 0.5
V cut-off was 5400 s for a 25 mA cm\(^{-2}\) pulse. There was no permanent voltage loss after 50,000 pulses at pulse currents below 25 mA cm\(^{-2}\). The cell capacitance was estimated to be 13.5 mF cm\(^{-2}\).

The pulse capability will depend strongly on the internal resistance of the cell, which is directly related to the relative humidity. Below 40% RH, the pulse capability is significantly decreased while at over 80% RH, the pulse power capability can double.

4. Hydrogen storage and generation

4.1. Hydrogen generation via decomposition of sodium borohydride solutions

As described, the goal for these microfabricated fuel cells is passive, ambient temperature operation. Hydrogen storage in the form of stabilized aqueous solutions of sodium borohydride (NaBH\(_4\)) is one option that meets these criteria. When sufficient base is added to raise the solution pH to \(\approx 14\), these solutions are stable at room temperature for several months. However, when brought in contact with a suitable catalyst, they readily decompose according to the reaction:

\[
\text{NaBH}_4 + 2\text{H}_2\text{O} \rightleftharpoons 4\text{H}_2 + \text{NaBO}_2
\]

Sodium borohydride is readily soluble in water, and solutions of over 30 wt.% NaBH\(_4\) can be made at room temperature. For a 30 wt.% solution, stabilized with 10 wt.% NaOH, the following theoretical energy densities can be calculated: 2337 mW h cm\(^{-3}\) (8.41 \(\times\) \(10^9\) J M\(^{-3}\)) and 2091 mW h g\(^{-1}\) (7528 J g\(^{-1}\)). This is equivalent to \(\approx 7\) wt.% H\(_2\). The borohydride system also offers distinct advantages compared to the metal hydride systems discussed below. The primary advantage is that the concentrated solution maintains roughly 35% RH at the fuel cell anode, thus providing a continual source of water vapor to the fuel cell. This has a very distinct benefit in maintaining higher electrolyte conductivity, which is especially important for pulse power delivery.

The simplest design for a hydrogen generator for the microfuel cell consists of a small well (i.e. an opened chamber) etched into a wafer to contain the borohydride solution, which is injected into the well with a syringe when the fuel cell is activated. The decomposition catalyst is printed onto the bottom of the well. The well is capped with the microfuel cell, with the underside of the microfuel cell substrate exposed to the hydrogen that bubbles up from the catalyst at the bottom of the well. A relatively long and small diameter vent through side of the well, above the solution level, allows air to be exhausted when the borohydride solution is injected, and maintains the hydrogen pressure at slightly above ambient, regardless of the relative rates of hydrogen generation by the decomposition reaction and hydrogen consumption by the fuel cell.

Varying the depth of the well for the borohydride solution allows the amount of energy stored to be varied. The obvious drawback of this system is that it is orientation dependent, the fuel cell must be held in an orientation that permits the borohydride solution to contact the decomposition catalyst and that only allows hydrogen and water vapor to be vented to the anode. We are currently working on more advanced designs that would be orientation independent and would incorporate a check valve on the hydrogen vent while remaining completely passive and still be readily manufactured.

A borohydride generator of the simple type was fabricated with a solution volume of 0.6 cm\(^3\).
microfabricated fuel cell bonded to the generator was continually operated at 0.5 V for over 90 h on one charge of borohydride solution. (Polarization curves with the attached hydrogen generator were essentially the same as those generated from hydrogen supplied by a tank.) Over this period, the current produced was monitored and integrated. The integrated current produced of 1822 coulombs was over 67% of the theoretical value for complete decomposition of 0.6 cm³ of the 20 wt.% NaBH₄ solution used. The fuel cell was still operating at the end of the 90-h period; however, the power output had dropped to about 25% of the initial value. Considering that the generator is not sealed, but vents excess hydrogen through a small opening, the fuel utilization achieved in this experiment is very promising.

Higher utilizations can be achieved by operating the fuel cell at constant current.

4.2. Hydrogen storage in metal hydrides

The advantages of storing hydrogen in metal hydrides include a high volumetric energy density with no operational dependency on orientation. A major goal of this effort was to produce a metal hydride material that is tailored to this micro fuel cell application, with an equilibrium pressure near atmospheric pressure at room temperature, and that can be applied in a thick film fabrication process. Integrated devices with energy densities on the order of 500 mW h cm⁻³ (1.8 × 10⁹ J M⁻³) for a 50 mW h (180 J) storage capacity should be feasible using this approach.

LaAlₐ₀.₃Ni₄.₇ hydride material with an additional surface modification has been formulated into a thick film printable ink with very low binder content. A second member of the AB₅ family of hydrides, CaNi₅, has also been evaluated. For both hydrides, the binder content was on the order of 1 wt.%, allowing for high volumetric energy density. The surface modification prevents deactivation of the hydride material. Printed inks remained active after over 5 weeks exposure to room air, at which time the tests were stopped. This is an important result because often these materials passivate on exposure to air or water, and can only be re-activated for hydrogen storage by exposure to high hydrogen pressures. As it is impossible to expose material contained within the fuel cell structure to high hydrogen pressures, a non-passivating hydride material is required.

It is also important to show that the hydride material can be repeatedly charged with hydrogen and discharged without loss of capacity. An automated Sievert’s apparatus was used for hydrogen sorption/desorption testing of up to six samples simultaneously. Various hydride powders and inks have been subjected to repetitive sorption/desorption testing consisting of 10 minute exposure to ≈133 kPa (1000 torr) H₂ (sorption step) followed by 600 s exposure to vacuum (desorption, pressure = 1.3 Pa (10 millitorr)). SEM micrographs after 1000 cycles showed no change in particle size, and no change in the adhesion of the ink to the substrate. These tests have been extended to over 4000 cycles without any significant change in the total amount of hydrogen stored, or in the rate at which hydrogen is adsorbed or desorbed. Over the same period, the ink based on the CaNi₅ hydride has lost ≈15% of its original hydrogen storage capacity.

Printed films of the LaAl₀.₃Ni₄.₇ ink have been used to provide hydrogen to small, conventionally fabricated fuel cells. In the first experiment, a constant 20 mA current was drawn from the fuel cell, while the cell potential and the hydrogen pressure above the hydride block were monitored, as shown in Fig. 9. Despite the fact that in this experiment, the fuel cell and the hydride

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Fig. 9. Small conventional fuel cell potential and pressure above hydride (LaAl₀.₃Ni₄.₇) storage block while maintaining 20 mA current output. The fuel cell is based on a Nafion® 117 film, with Pt/C printed electrodes of one square centimeter.
block were connected by $\approx 5$ cm of 0.32 cm OD tubing, the fuel cell maintained a constant potential until the pressure dropped to $\approx 8$ kPa (60 torr). The hydrogen consumed during this test represented over 90% of the hydrogen initially stored in the hydride material. With the extremely close coupling of fuel cell and hydride material that will occur in the microfabricated devices, even higher utilizations should be possible. It also is important to note that the potential was essentially constant until the very end of the test; the sloping equilibrium pressure of this hydride material was not reflected in a varying fuel cell performance under these conditions. In Fig. 10, a complete polarization curve for the fuel cell is shown. A current output of over 200 mA was achieved without reaching a limiting current, indicating that the hydrogen desorption rates from this hydride ink are more than sufficient for the microfabricated fuel cell, which is expected to operate at currents on the order of 10 mA.

5. Summary

Aspects of the design, materials and fabrication of a microfabricated fuel cell have been presented. An estimate of the performance of these devices is summarized in Table 1, with a comparison to a Li−MnO$_2$ primary battery of similar voltage, size and energy storage. The interesting advantages of the microfabricated fuel cell as compared to the battery lie in the ability to fabricate the fuel cell on the same substrate as other microelectronic, microelectromechanical or microfluidic devices, in the ability to independently tailor the design for a desired power and energy storage combination and in the ability to provide peak power.

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Table 1
Comparison of microfabricated fuel cells and a Li−MnO$_2$ coin cell

<table>
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<tr>
<th></th>
<th>Micro fuel cell $^a$</th>
<th>Li−MnO$_2$ coin cell Duracell 2016</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal voltage</td>
<td>3 V</td>
<td>3 V</td>
</tr>
<tr>
<td>No. of cells</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>Weight</td>
<td>1.7 g</td>
<td>1.8 g</td>
</tr>
<tr>
<td>Dimensions</td>
<td>2.7 × 1.8 × 0.2 cm</td>
<td>2 cm dia., 0.2 cm thick</td>
</tr>
<tr>
<td>Capacity</td>
<td>60 mA h/cell (216 J/ cell)</td>
<td>75 mA h (0.2 mA rate) (270 J)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 mA h (1 mA rate) (216 J)</td>
</tr>
<tr>
<td>Energy</td>
<td>200–300 mW h (720–1080 J)</td>
<td>6 mW</td>
</tr>
<tr>
<td>Maximum continuous power</td>
<td>3–15 mW (depends on %RH)</td>
<td>30 mW (depends on %RH)</td>
</tr>
<tr>
<td>Peak power (10 ms pulse)</td>
<td>50–100 mW (depends on %RH)</td>
<td></td>
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$^a$ Values for micro fuel cell based on single cell and three cell structures scaled to yield a 3 V device.
implied of DARPA, or the US Government. This work summarizes the combined efforts of a number of students, engineers and postdoctoral researchers over the past 5 years. In particular the authors would like to acknowledge the efforts of Ms. Laurie Dudik, Dr. Arunkumar Venkatesan, John Staser, Andrew Swann, Ms. Lynn Chen, Hyoung-Juhn Kim, Dr. Snezana Gojkovic, Ms. Liangyuan Chen, Xi Shan and Kenneth Yee, and Professor Joe Payes.

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