NEXT GENERATION MICRO-FUEL CELLS: FUEL STORAGE, CONTROL, AND POWER GENERATION

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The quest is on for high power and energy density power sources at ever smaller sizes for applications ranging from on-chip sensors to insertable pharma-delivery to flying microrobots. Fuel cells have often been touted as a next generation power source that can deliver both high power and energy density (in part because they do not have to carry the oxidizer on-board, using the oxygen in air). However, shrinking fuels to the microscale is fraught with problems. Unlike batteries that carry both redox reactants whose products remained within the battery, and which do not need ancillary devices (save for the container and electrodes), fuel cells additionally need a means to supply the fuel, oxygen, exhaust the products, and control the hydration level throughout the device. Moreover, fuel cells need a means to control the fuel and oxygen delivery with changes in electrical load, which often use elaborate mechanical and electrical control systems. Therefore, it is difficult for many fuel cells to handle huge changes in load. The main problems for microscale fuel cells, therefore, are how to supply fuel with high energy density, without using large ancillary systems that consume significant amounts of power, and for the fuel cell to respond to large changes in electrical load, in varying ambient temperatures and humidities.

In spite of these challenges, proton exchange membrane (PEM) micro-fuel cells have now reached less than 10 microliters in total volume, as shown in Figure 1, including the fuel, PEM, and ancillary systems, with instantaneous peak power density of 360 W/l and an energy density over 250 W·hr/l, and are headed to instantaneous power density higher than 1000 W/l and an energy density above 500 W·hr/l. These fuel cells also have a dynamic range of over three orders of magnitude of operation from micro-Watts (steady-state) to milli-Watts (steady-state), with 10 mW instantaneous peak power. However, to achieve this dynamic range, energy, and power densities, the membrane electrode assembly, control system, and fuel storage all have to be designed and optimized to maximize fuel storage, without having large fuel and power control systems, and without using parasitic power.

The fuel that is used in these micro-fuel cells are metal hydrides (such CaH2, LiAlH4, NaBH4, etc.) with water supplied either through a separate chamber or through the air to generate hydrogen on contact with the hydride, with total possible energy densities near or over 700 W·hr/l accounting for stored water as shown in Table 1, and over a 1000 W·hr/l with scavenging water from the air.

However, the hydrides will react nearly instantaneously with water in any form to produce hydrogen gas, regardless of its pressure, which can cause the fuel cell to over pressurize and burst. Therefore the amount of water brought into contact

![Figure 1](image-url)

*Figure 1* – Pictured on left is a complete micro-fuel cell of less than 10 microliters in volume, that includes, water reservoir (showing two ports to load water, which are sealed by drops of RTV sealant), a control valve, metal hydride fuel reservoir, and the actual fuel cell membrane electrode assembly. On right is the exploded and assembly cross-sectional view of the fuel cell with photos of the individual components.
with the dry hydride has to be accurately controlled to supply a power of micro-Watts and lower, then switching to milli-Watts of power and larger. Controlling the hydrogen generation rate over 3 orders of magnitude with changes the electrical load is a challenge in itself, all without consuming electrical power, since the lower limit of virtually any parasitic power would be unacceptable. In addition, the volume of the control system must be much less than the total size of 10 micro-liters.

Table 1: Some hydrogen generation results for CaH$_2$ and LiAlH$_4$ for an inline (Reactor 1) and sideflow (Reactor 2) micro-reactor designs. Note the final row includes the expansion due to hydrate formation.\(^1\)

<table>
<thead>
<tr>
<th>CaH$_2$ (≥ 97%)</th>
<th>LiAlH$_4$ (≥ 95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor 1</td>
<td>Reactor 2</td>
</tr>
<tr>
<td>Weight of hydride (mg)</td>
<td>51</td>
</tr>
<tr>
<td>Water (µL)</td>
<td>42.3</td>
</tr>
<tr>
<td>Hydrogen (mL)</td>
<td>57.3</td>
</tr>
<tr>
<td>Volume of the reactor (µL)</td>
<td>56</td>
</tr>
<tr>
<td>Yield</td>
<td>99.7%</td>
</tr>
<tr>
<td>Volume density (mm$^3$ H$_2$/mm$^3$ reactants)</td>
<td>828.7</td>
</tr>
<tr>
<td>Volume density with byproducts volume expansion (mm$^3$ H$_2$/mm$^3$ reactants)</td>
<td>695.9</td>
</tr>
</tbody>
</table>

Therefore, we developed a combined gas pressure regulator, liquid water controller that does not consume electrical power, in a volume of ~ 10 nl.\(^1,5\) As shown in Figures 1 and 2, we use a movable diaphragm that responds with increasing hydrogen pressure, closing off the port to the water reservoir. For proper functioning, the residual stress in the polyimide diaphragm, which is determined in part by the bonding temperature, restores the diaphragm position to the neutral position with decreasing pressure, which is also balanced by water tension in the gap between the diaphragm and water reservoir walls, and the evaporation through the ring of holes seen in Figure 1. The water vapor that evaporates through the holes enters the hydride reservoir, and then permeates through any metal hydrate from previous water-hydride reactions. The water that reaches the dry hydride is then assumed to immediately react, evolving hydrogen gas that diffuses through the remaining dry hydride through to the membrane electrode assembly (MEA), increasing the hydrogen pressure until the membrane deflects and closes off the water port. Hydrogen pressure is reduced through consumption by the fuel cell. When the pressure drops low enough for the water port to reopen, the cycle repeats. The control is not strictly on-off as described. As hydrogen pressure increases, the gap closes, reducing the amount of water available to evaporate, slowing the hydrogen generation rate, and vice versa. Therefore, the response is smoother than bang-bang control.

Figure 3 shows current load following by the micro-fuel cell to switching from zero (open circuit ~ 1 V held by a potentiostat) to a relatively high load (0.3 V held by potentiostat).

Another key problem with shrinking the size of a MEA is that the hydration level of the proton exchange membrane cannot be easily controlled. The MEA dries out if the ambient humidity is low.
Thus, if the PEM is made from the usual material, Nafion\textsuperscript{6}, which can dramatically lose proton conductivity as the humidity level drops, the fuel cell can cease to properly function. To solve this problem, a new type of silicon-based PEM was developed that has an order of magnitude higher proton conductivity than Nafion-based proton exchange membrane electrode assemblies.\textsuperscript{6} Figure 4 shows a cartoon of the PEM on the left side, and an SEM image of the nanopores within the silicon on the right side. The nanopores are functionalized with sulfonate groups to allow hydration with water with deprotonated walls to enhance proton transport within the pores. The silica caps help prevent evaporation of water from the pores. The result of this silica addition, shown in Figure 5, is that the proton conductivity is an order of magnitude higher at high relative humidity (RH\%), and over two orders of magnitude higher at low RH\%.

While the proton conductivity is actually much higher than Nafion in the PEM, and the hydrogen gas production can be controlled with load, one of the drawbacks of the current design is that at steady-state the power output is limited by the hydrogen generation rate, which is primarily limited by the water diffusion rate through the metal hydrate layer that forms, particularly after long term operation. Figure 6 explicitly shows this limit being reached at 0.6 V. Peak currents and power can be much higher for shorter transients, such as seen in Figure 3. New reactor designs and fuel packing schemes can limit the effect of hydrate formation on the hydrogen generation rate, to increase the dynamic range of steady-state current production of these micro-scale fuel-cells.

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