

# **SMALL BATTERY – FUEL CELL ALTERNATIVE TECHNOLOGY DEVELOPMENT**

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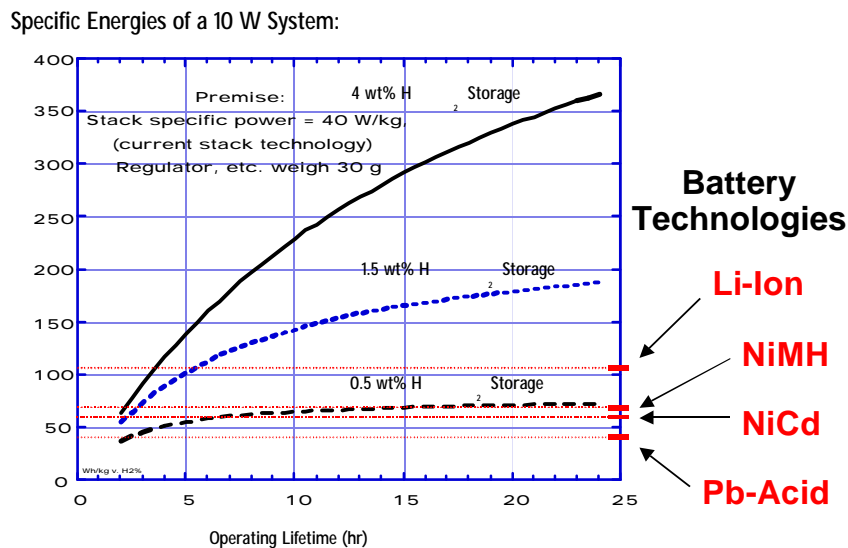
## **Abstract**

A compelling market segment for the introduction of hydrogen fuel cells is in small battery types of applications. While in other applications (e.g. transportation), fuel cells need to compete with relatively effective and low-cost technologies, batteries are expensive and have low energy densities. Even with modest hydrogen storage densities such as metal hydrides, fuel cells can provide higher energy densities than batteries and the values can increase substantially further with an increase in the energy to power ratio of the system (which is fixed for batteries). However, the fuel cells will still have to compete with batteries on reliability and cost. As such, the typical polymer electrolyte fuel cell system with its heavy reliance on subsystems for cooling, humidification and air supply would not be practical in small battery applications. Instead, the fuel cell system will ideally be simple, inexpensive, and reliable. In response, Los Alamos National Laboratory (LANL) conceived of a novel, passive, self-regulating, "air-breather" fuel cell stack that requires no moving parts (fans or pumps) and still maintains sufficient hydration of the polymer electrolyte membrane to provide stable and reliable power. The Hydrogen Program is funding the Los Alamos effort in a partnership between LANL and DCH, Inc. to further technological development and understanding of the air-breather in order to attain a commercially viable portable fuel cell system.

## **Introduction**

Despite the ever increasing attention and funding that polymer electrolyte fuel cells are attracting, the technology has not yet managed to become a factor in the two most significant areas of

development, transportation and stationary power. This may primarily be due to the entrenched and relatively successful and inexpensive technologies they are trying to displace. Current battery technologies, on the other hand, are not entirely satisfactory for many portable applications due to a number of factors. Depending upon the particular type of battery, these factors may include low energy densities, rechargeability and cycle-life issues, stability, cost, operation temperature, and environmental or safety issues. As such, the potentially superior energy densities of fuel cells may provide a competitive advantage in small battery type applications provided they can satisfy the other relevant criteria of cost, reliability, etc. Figure 1 compares the specific energies (Whr/kg) of several rechargeable battery technologies with a fuel cell system, such as the one described here, using hydrogen storage systems of various gravimetric hydrogen densities. Some of the more common and more promising battery technologies are shown in the figure, such as advanced lead-acid (Pb-Acid), nickel-cadmium (NiCd), nickel metal hydride (NiMH) and lithium ion (Li-Ion). As seen, even a modest hydrogen storage capability of 0.5 wt% hydrogen is quite competitive with the battery technologies other than Li-Ion. Higher hydrogen storage densities are shown to provide substantially greater specific energies, especially as the operating lifetime increases. Since the energy and power sources are two separate components in the fuel cell system, the specific energy and energy density of the system increases simply by increasing the hydrogen storage capacity. In the case of batteries, the electrodes are both the energy and power sources so the energy densities are fixed, as depicted by the flat curves for the batteries in the figure. If the higher hydrogen storage capacities can be realized in a safe and user-friendly technology, the fuel cell system has a clear advantage over the battery technologies for applications where longer operating lifetimes are desirable.



**Figure 1 - Relative Specific Energies of Battery and Portable Fuel Cell Technologies.**

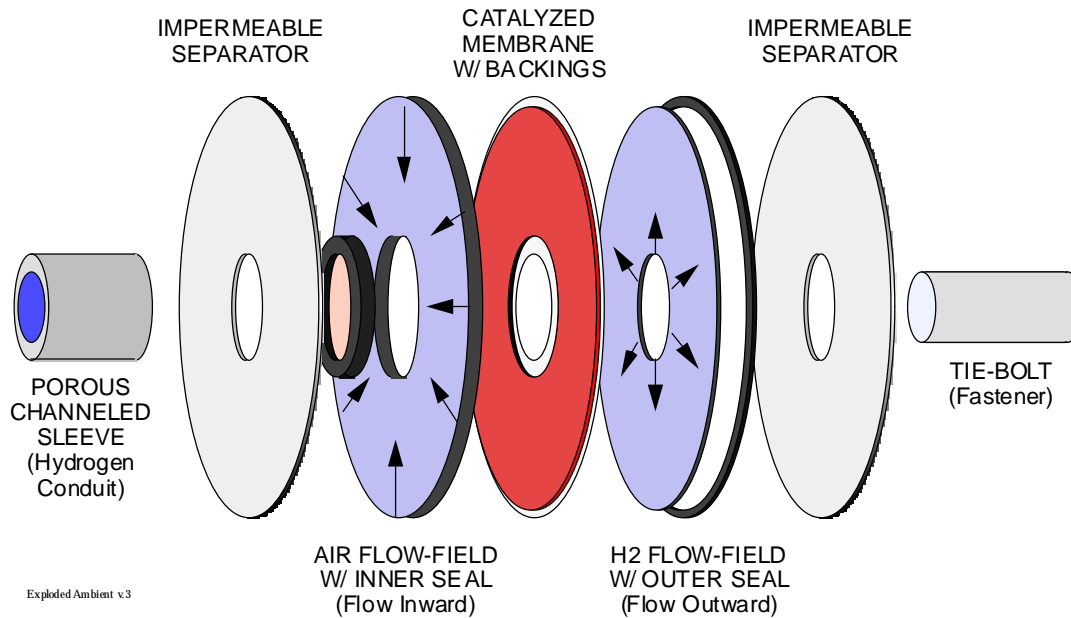
On the other hand, such portable power applications will still require a combination of reliability, simplicity and relatively low-cost. As such, the fuel cell system will probably not be able to

satisfy these criteria if peripherals such as humidification, and cooling or reactant flow fans and the attendant electronics and controls that are typical of polymer electrolyte fuel cell systems are required. Ideally, the system would operate effectively with no active humidification, no active cooling, and no pressurization or forced flow of the cathode air. As a consequence, our group at LANL investigated the possibilities of developing a simple system that was inherently stable and self-regulating. The scheme that we arrived at is passive and relies on diffusion limited oxygen access to maintain a positive water balance. The oxygen in the air must diffuse into the stack from the periphery of the flow-field plates. For this reason the stack is often described as "air-breathing." Given that the oxygen must diffuse in, twice as much water (as there are two molecules formed per O<sub>2</sub> that reacts) must diffuse out to maintain an even balance. While it first appears that a surplus of water is obtained, the fuel cell stacks quickly heat up and the water removal is greatly facilitated. Overall, the balance remains fairly even such that the polymer electrolyte membranes do not dry out, even at relatively high continuous operation temperatures (+70 C). Thus, the diffusion supply scheme results in simple stacks with reliable and stable performance. A unique fuel cell stack geometry is used to optimize the diffusion limited configuration as well as to greatly simplify the configuration.

## **Discussion**

### **Air-Breather Fuel Cell Stack Scheme**

Since the oxygen needs to diffuse in from the periphery of the cathode flow-field plate, the fuel cell assumes the unique configuration shown in Figure 2 that utilizes circular flow-field plates with an annular hydrogen feed manifold and a single tie-bolt extending up through the central axis of the stack. With this geometry, the hydrogen supply to the unit cells is radially outward, and the air supply is from the periphery inward. This configuration has several advantages. The entire periphery is free to air access and allows greater heat conduction to enhance cooling and the diffusion path lengths are minimal for both the hydrogen from the annular region and the oxygen from the periphery. Furthermore, all of the components in the stack (e.g., the flow-fields, seals and membrane/electrode assemblies), are radially symmetrical, so part fabrication is simple and the entire system is potentially low-cost. The use of a single tie-bolt decreases the footprint and helps provide a configuration that is compact and lightweight. All that is needed to operate this type of fuel cell stack is a low pressure hydrogen supply that can be provided from a pressurized source via a low-pressure regulator.



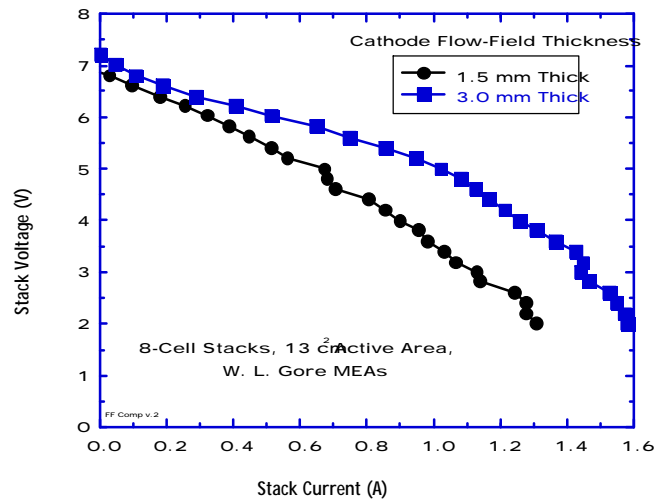
**Figure 2 - Configuration and key components of a unit cell in an air-breather stack.**

The unit cells are typically 2" (5.1 cm) in diameter with active areas of about 13 cm<sup>2</sup>. End-plates compress the collection of unit cells together with the use of the tie-bolt projecting up through the middle. Jacketing the tie-bolt is a porous, hydrophilic, channeled sleeve that provides alignment for the unit cell components and serves as a conduit for the hydrogen to reach the inner edge of the hydrogen flow-fields. Hydrogen feed is dead-ended, although provision is made for an initial purge. The reactant flow-fields are typically reinforced carbon paper (e.g. Spectracarb, from Spectracorp, Lawrence, MA). Seals are located at the inner edge of the air flow-field and the outer edge of the hydrogen flow-field. The flow-fields bracket the membrane/electrode assembly (MEA), which consists of a catalyzed polymer electrolyte membrane from W. L. Gore & Assoc. sandwiched between two gas diffusion backings from E-TEK (Natick, MA). The W. L. Gore MEAs used here are quite thin (ca. 20 μm) and the catalyst layers tend to take up a substantial amount of water. These factors result in improved hydration and performance under the relatively difficult operating conditions. Stainless steel foil separators, that are typically 0.010" (0.25 mm) thick, prevent the reactants in the back-to-back flow-fields from mixing. In multi-cell stacks, the separators are of a larger diameter than the flow-fields to provide cooling fins, which gives the stack the appearance of a finned tube.

When the cells are stacked, not only do the structures heat up more but water accumulation in the annular region actually becomes a problem. Since the hydrogen supply is dead-ended, condensate can collect undisturbed and block the hydrogen from accessing the cells furthest from the hydrogen supply. The accumulation can be prevented by introducing a wicking material in the annular region that draws the condensate away from the downstream cells (Wilson and Neutzler 1997).

Not surprisingly, cell performance is substantially affected by the thickness of the cathode flow-field because oxygen must diffuse in from the periphery through this structure. While the thicker flow-fields provide high powers at low temperatures, too much water is lost at higher temperatures. Since under continuous operation a multi-cell stack naturally runs much warmer than a single cell (ca. 60 C vs. ca. 30 C), flow-fields that are too thick allow the cells to dry out.

Computer modeling simulations of the water vapor concentration profiles anticipate the trade-off between cathode flow-field thickness and stability. For example, it is predicted that a significant portion of the active area is still water vapor saturated at 60 C with 1.5 mm thick flow-fields, but with a 4.5 mm thick flow-field, water vapor saturated conditions are not achieved anywhere within the cell even as low as 50 C ( Neutzler 1995). Thus, as is observed in the laboratory, stacks with the excessively thick flow-fields become unstable and dry-out as they heat up. Three millimeter thick flow-fields appear to provide a compromise between stability and output.

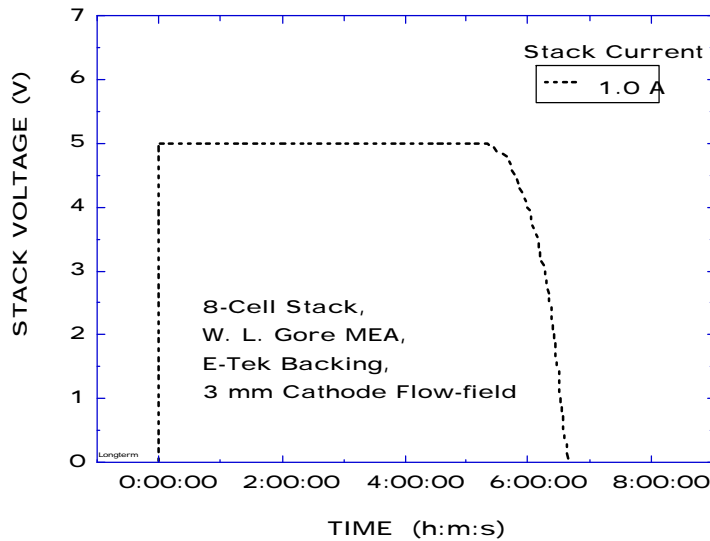


**Figure 3 - Effect of Flow-Field Thickness on Air-Breather Stack Performance.**

Figure 3 depicts polarization curves for two continuously operating 8-cell stacks using either 1.5 or 3 mm thick cathode flow-fields at an ambient pressure of 0.76 atm (the laboratory is at an altitude of 7,300 ft or 2,250 m). The 4.5 mm thick example is not shown because the stack dries out when operated continuously at 5 V, much as predicted by the computer simulations. The figure illustrates that the 3 mm thick flow-fields provide more power than the 1.5 mm as well as sufficient stability (Wilson et al. 1996).

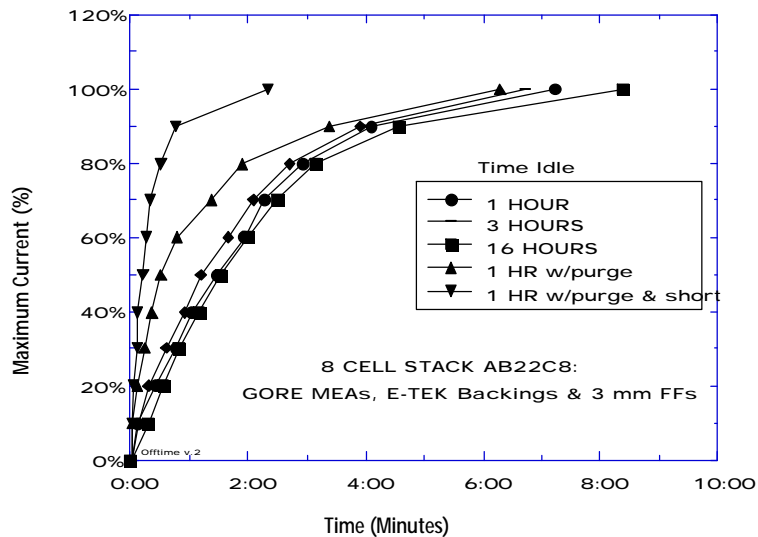
### Utility of the Air-Breather Fuel Cell Stack

In many applications, a stable fuel cell power supply may be desirable. Figure 4 depicts the voltage output of an 8-cell air-breathing stack operating on a commercial portable metal hydride canister (a BL-30 from HCI, Inc., Littleton, CO) at a constant current of 1 A. After running continuously for some time at 5 V on test station hydrogen, the cell is switched over to the hydride canister at  $t = 0$ . As shown in the figure, the fluctuations about 5 V are quite small running on the hydride cylinder for the first 5 - 6 hours, at which point the hydrogen supply diminishes and the cells start becoming starved for fuel.



**Figure 4 - Air-Breather Fuel Cell Stack Stability using a Metal Hydride Canister.**

Another factor of consideration is the rapidity with which sufficient power for the application can be attained. A certain amount of warm-up is required of the air-breather before the maximum power is attained. If initially, however, a short pulse of high power is required for start-up of the device, the fuel cell can often supply the required power pulse right off because of the extra oxygen in the flow-fields of an idle stack. For example, we have run a computer laptop off of two 10-cell stacks. The greatest power draw of the laptop is right at the start when the hard drive and other circuitry powers up to speed. Normally, the cells would need to be warmed up to provide this level of power, but the laptop can still be started with cold cells because of the second or so of power surge that can be provided. Once the diffusion limiting oxygen profile is re-established the power quickly drops back to that which is normally anticipated and starts its climb as the system warms-up. Figure 5 shows how quickly an 8-cell stack can recover from idle under a number of different circumstances. The brief initial power surge described above is not depicted. Three of the curves depict the response after the cell has been shut-down and disconnected from hydrogen for 1, 3, and 16 h. A large part of the lag appears to be due to the time required for hydrogen to displace and diffuse through the air in the annular region upon restart. In this case, the hydrogen pressure is about 5 psig. Quicker responses can be obtained using higher pressures, or, as also shown in the figure, a purge of a second or two substantially increases the initial rate of recovery. If the brief purge is combined with electrically shorting across all of the cells of the stack for a second or two, the cell rapidly recovers, as is shown in Figure 5. The exact reasons for the quicker response are not clear but it may be a combination of heat and water formation and contaminant removal.



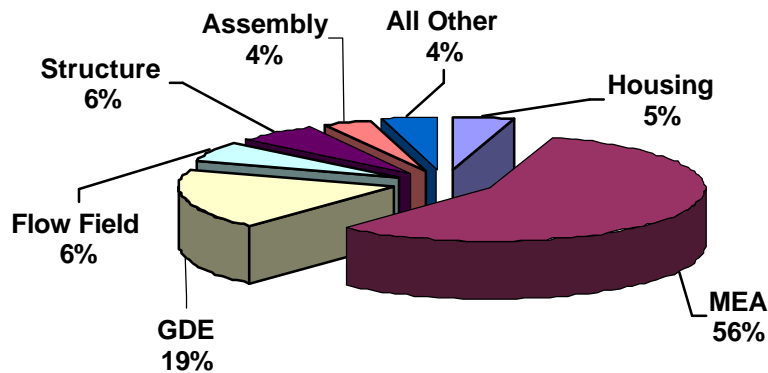
**Figure 5 - Recovery from idle for an Air-Breather Stack.**

## Commercial Design and Development

Improvements in the design and performance beyond that described above are desirable to facilitate DCH, Inc.'s efforts to commercialize the technology. Many of the details are proprietary, but for one example, a primary objective of the redesign was to replace or eliminate the porous channeled sleeve depicted in Figure 2. This component is relatively expensive, requires post-machining to provide the channels and the proper inner diameter, and is a relatively soft material that was not particularly effective in assuring the proper alignment of the separator plates and flow-fields. Several approaches are feasible, DCH is using a scheme that is advantageous for production and LANL is using individual "hubs" for each separator plate that provide alignment, hydrogen flow, wicking passages and also facilitate disassembly for swapping out components. Another subtle alteration is in making the diameters of all of the separator plates uniform such that there is a short fin per cell rather than the alternating large fin / no fin arrangement previously used. The change does not appear to affect performance and also decreases the footprint as well as the number of different parts required.

The investigation of alternative materials is of substantial concern and is motivated by either broadening the supplier base or to lower part costs. Figure 6, provided by DCH, Inc., illustrates the relative costs of the air-breather components at nominal levels of production. As can be seen, the cost of the MEA material dominates and hence is of primary concern and significance. Unfortunately, the potential alternative materials that have been tested do not provide as high performance and in one case the product line has been discontinued. High MEA and GDE (gas diffusion electrode) costs is a problem that has long stymied polymer fuel cell development for all applications. At this point, there is little competition for the MEA and GDE suppliers and

production is still at a modest scale so high costs will probably be a factor until more competitors emerge and/or the size of the market increases substantially.



**Figure 6 - Cost Breakdown for Air-Breather Stacks (from DCH, Inc.)**

While not particularly expensive compared to the MEAs and GDEs, alternatives to the porous flow-field material could still make an impact on costs and ease of assembly. One early exercise considered replacing the porous material with rigid conductive plates with cross-hatched air flow-field channels in place of the porous flow-field. In principle, such a structure could eventually be molded with O-ring grooves and other features at a relatively low cost. However, the performance of a 12-cell stack with such plates was quite poor and erratic. Apparently, some free convection was occurring in the channels contributing to the instability and drying out of the MEA. Also, the limited oxygen access to the MEA in those regions over the flow-field islands limited even the baseline performance compared to the uniform access provided by the porous material. Although the results were poor, the experiment validated the importance of the diffusion-based reactant / water management approach.

### **Conclusions**

The best opportunities for the meaningful commercialization of fuel cells should exist in the most forgiving markets where current technology is relatively expensive and is perceived as inadequate. While many small battery type applications meet these criteria, the fuel cell technology will itself need to be robust, reliable, sufficiently low-cost and versatile. As such, the passive, self-regulating, "air-breather" fuel cell stack has advantages over most traditional polymer electrolyte fuel cell systems in that it fundamentally requires no auxiliaries (other than a hydrogen supply) and still maintains sufficient hydration of the polymer electrolyte membrane to provide stable and reliable power. The performance and utility of the diffusion limited flow-field approach integrated into the circular unit cell geometry has been demonstrated with modest sized units. In conjunction with DCH, stack design improvements and packaging development should create a viable commercial fuel cell product



## Future Work

Future work entails the continuing investigation of lower cost stack fabrication methods and materials. The issues involved with scaling of the air-breather stacks to higher power levels will also be explored. These issues involve the thermal gradients and hydrogen supply effectiveness using the longer structures. The build-up of inerts in the hydrogen may become more pronounced with the additional membrane surface area. Strategies that have been formulated to combat these problems need to be tested and refined. One general approach is to tolerate the inert build-up but disturb the stagnant diffusional barriers. Another is to monitor the build-up using sensors and perform purges as and if needed. DCH has licensed and successfully commercialized state of the art hydrogen sensor technologies including the Robust Hydrogen Sensor (RHS), from Sandia National Laboratories. This technology will be used as a starting point to integrate hydrogen sensors into a fuel cell stack control and safety system as many potential applications require some level of remote status monitoring and operability or safety assurance.

The packaging of the otherwise stand-alone stacks will need to be explored on a basis of intended applications, cost allowances, sophistication of the control and power modulation electronics, etc. Options range from simple housings that cloak the stack to integrated modules where hydrogen supply, electronics, and the the air-breather stacks are all integrated. Ideally, such enclosures can be designed such that the various elements are integrated in a symbiotic manner that maximizes system effectiveness.

The major programmatic objective for DCH and LANL for the first year is to design, fabricate and test 50W modular air-breather fuel cell stacks incorporating RHS technology for hydrogen monitoring and feedback control. Next year, the target is to package the most successful 50 W stack and system designs into 300 W modules that provide user selectable voltages or currents depending upon the desired applications.

## Acknowledgements

We wish to thank the Hydrogen Program for supporting this project. The collaborative effort with DCH and the funding for LANL from the Hydrogen Program is primarily due to the efforts of David Haberman of DCH, Inc. Mark Daugherty, the lead scientist at DCH on the air-breather, should be commended for an effective and successful transition of the technology from Los Alamos to DCH .

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