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SMALL BATTERY — FUEL CELL ALTERNATIVE TECHNOLOGY DEVELOPMENT

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Abstract

A compelling market segment for the introduction of 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 easier to compete with because they 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 should 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. Enable Fuel Cell Corp. (a subsidiary of DCH Tech.) has been partnered with LANL to further technological development and commercialize the air-breather. Development has reached the point where a 12 W system has officially become a commercial product. Nevertheless, understanding of the approach is continually improving and the design is being refined and adapted for various applications. It would appear that the primary factor now affecting market penetration is the fuel storage issue.

Introduction

Depending upon the fuel storage technology, fuel cell systems can provide substantially higher energy densities than similar-sized battery packs. Correspondingly, interest in fuel cells for portable power applications is rapidly increasing and now global electronics companies are pursuing the possibilities. In this program, LANL and Enable Fuel Cell Corporation are developing a unique low-power portable fuel cell and system inexpensive and reliable enough to eventually compete head-to-head with batteries in electronics-type applications. The advantage of this fuel cell system over current competing fuel cell designs is that it does not require the use of peripherals such as cooling or reactant flow fans and can operate effectively with no active humidification, no active cooling, and no pressurization or forced flow of the cathode air. The system is inherently stable and self-regulating. A passive scheme is used that 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_2 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 (+60°C). Thus, the diffusion supply scheme results in simple stacks with reliable and stable performance. To operate this type of fuel cell stack only a low pressure hydrogen supply is required which can be provided from a pressurized source (such as metal hydride canisters) via a compact low-pressure regulator.

Discussion

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 1 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 (Wilson 1996). 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 reactant flow-fields are typically reinforced carbon paper and membrane/electrode assemblies (MEA) are of conventional design. Seals are located at the inner edge of the air flow-field and the outer edge of the hydrogen flow-field. Stainless steel foil separators prevent the reactants in the back-to-back flow-fields from mixing. As shown in the right hand side figure, end-plates compress the collection of unit cells together with the use of the tie-bolt projecting up through the middle. The use of a single tie-bolt decreases the footprint and helps provide a configuration that is compact and lightweight. In multi-cell stacks, the separators can be of a larger diameter than the flow-fields to provide cooling fins, which gives the stack the appearance of a finned tube.

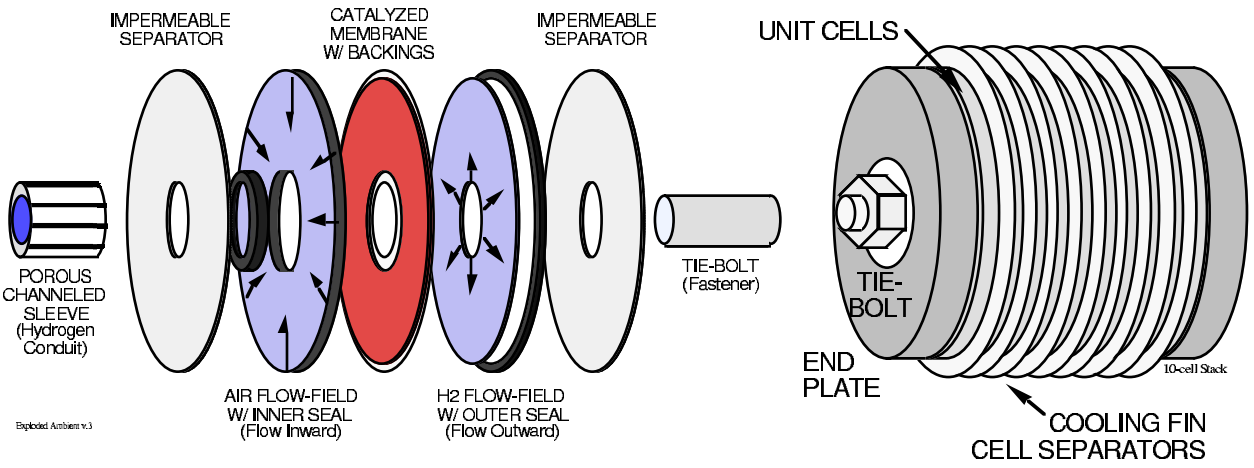

Figure 1 - Configuration and key components of a unit cell in an air-breather stack.

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 alleviated 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 as the stack heats up to higher temperatures, especially at the relatively high altitude of LANL (2,250m or 7,300'). The optimum flow-field thickness for both power and stability at LANL is about 3 mm, but can be greater at low altitude. With the high altitude, the ambient pressure is only about 0.76 atm. Not only is the oxygen partial pressure lower (and hence kinetics poorer), but the stacks also tend to run much drier because the higher volume fraction of water vapor that can occur results in a greater driving force for removing water from the stack. Another aspect of high altitude operation is that cooling by free convection is much less effective than at sea level, which naturally exacerbates the drying effect. For these various reasons, a stack that stably produces 25 W at LANL can produce up to 35 W at sea level while actually operating cooler, and excess water may actually be accumulated. Thus, more leeway is afforded designs provided they are operated at lower altitudes. Conversely, products that are oriented towards camping or backpacking impose even more stringent design limitations.

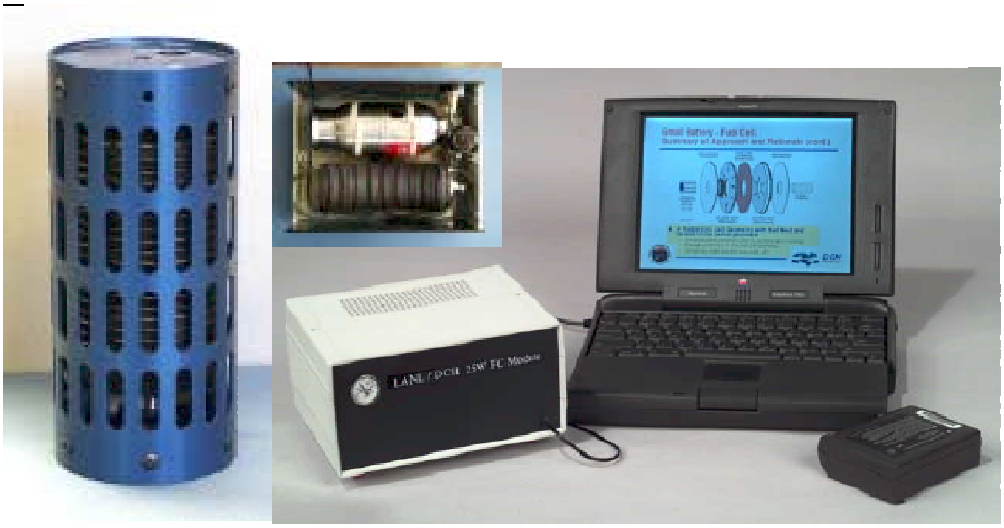

Figure 2 — Various Air-Breather Packages — The Enable Commercial Product and a Fully Integrated Module Operating a Laptop.

The versatility of the air-breather allows it to be packaged in various ways. Two examples are shown in Figure 2. On the left is the initial Enable FCC product which has recently become commercially available. As can be seen, the air-breather is mounted vertically and is protected by a shroud with elongated openings that allow air to freely convect upward and over the stack to provide cooling. While capable of more power, the stack is conservatively rated at 12 Watts at roughly 12 V and is design to be affixed atop the hydrogen supply in a tower configuration that is then suitable for supporting a camping lantern. On the right is a fully integrated module containing both the stack and a metal hydride canister, as is shown in the top view in the inset in Figure 2. A small pressure gage indicates the status of the fuel supply. Positioned side-by-side, air convection thermally couples the 36-cell stack and the hydride canister to provide cooling air for the stack and to heat the hydride to facilitate the desorption process. The module supplies 25 W at LANL's altitude and can operate the laptop shown scrolling through a slide presentation for almost 12 hours. Although the energy density of the system depends upon the stack power, at approximately 25W it works out to a relatively modest 75 Wh/kg (still better than most rechargeable battery technologies), because the metal hydride canister is at best only about 1% hydrogen by weight. The true promise of fuel cells will be realized only when more effective hydrogen storage technologies are developed. For example, the same system with 4% hydrogen storage would obviously yield a 300 Wh/kg package and operate the laptop for nearly 48 h.

Much of the effort over the past year has continued to concentrate on optimizing the air-breather design in improving performance, lowering component costs and facilitating manufacture. One of the simpler improvements is to use a more open annular region. The performance improvement is most likely attributable to better and more uniform access of the hydrogen to the entire inner edge of the hydrogen flow-fields. Since the system operates dead-ended, a certain amount of diffusion transfer probably has to occur as inerts accumulate in the hydrogen distribution network. In our particular experimental stack design at LANL, we simultaneously changed the design of the "hub" not only to open up the free area but also to improve the effectiveness of the inner edge seals for the air flow-fields. The individual "hubs" for each separator plate provide alignment, hydrogen and wicking passages for each cell and also facilitate disassembly for swapping out components. The hub also effectively replaces the porous channeled sleeve depicted in Figure 1, which was a particularly problematic component. Since the carbon paper air flow-fields can compress

substantially, the seal area basically varies as a function of the end-plate compression. Many times a cell or two in a stack would not seal until the entire assembly was further compressed, probably due to small differences in the various material thicknesses , compressibilities, etc. The seal design was modified to allow the hub to float, thus minimizing the effect of the variations. Since this change has been implemented, stacks have all sealed the first time, which naturally improves manufacturability and reproducibility.

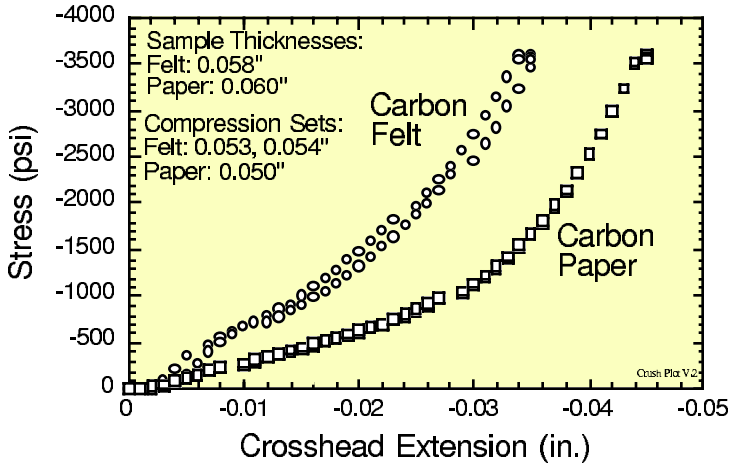

Figure 3 — Compressibilities of carbon papers and felts.

Much of the optimization is of a proprietary nature but the issue of accommodating the compressibility of the carbon paper air flow-fields leads to an example of component optimization vis-à-vis performance and manufacturability. Carbon papers have been a staple component in fuel cells for many years but they are relatively expensive. More recently, carbon felts have become commercially available, and already they appear to be less expensive. As shown in Figure 3, the felts are less compressible and take less of a set than a paper of the equivalent thickness, which improves the manufacturing aspect. On the other hand, edgewise permeability measurements using the classic Stefan Diffusion Tube configuration suggests that the papers are slightly more permeable. Thus, a somewhat thicker sheet will in principle be needed to provide the same performance. As is often the case, changing one component then has ramifications on the other elements in the system, and optimizing the system fully around price and performance becomes all the more difficult because of it.

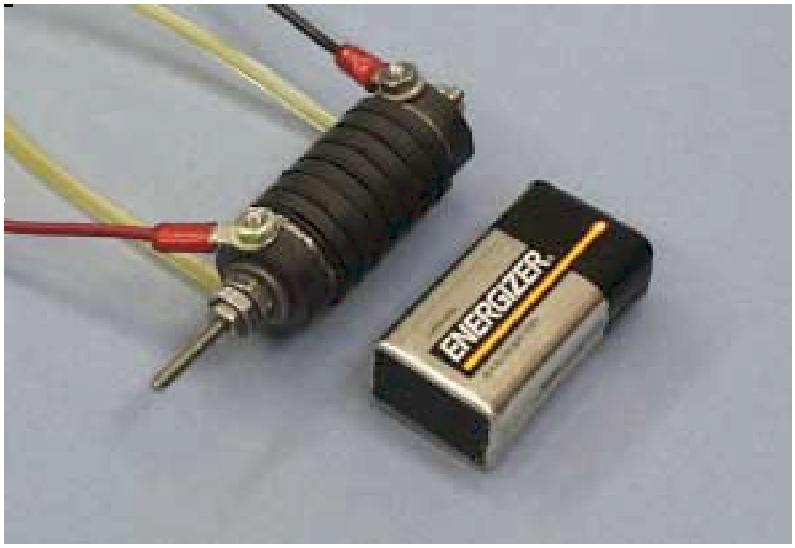

Figure 4 — A Miniature 1 W Air-Breather Alongside a 9 V Alkaline Battery.

The global electronics industries that are entering the fuel cell arena are primarily interested in personal electronics applications such as cellular phones, hand-held computers, etc. The power requirements are more on the watt level rather than the tens of watts appropriate for the air-breather scale we have thus far been employed. Figure 4 is a picture of our first effort on a watt-level air-breather. While successful, the design was rather primitive and hence not of the possibly highest performance and also not particularly amenable to commercialization. The annular and tie-bolt region is very cramped and it appeared that there were hydrogen access limitations. One of the challenges on such a small scale is to obtain a reasonable fraction of active area with such small diameters because so much of the plate area is lost to seals, the tie bolt and the hydrogen feed region. The area taken up by the outer (hydrogen) seal is roughly equal to the active area. Although the current densities are already higher than the larger stacks (as expected), further performance increases should be readily attainable as the designs are improved.

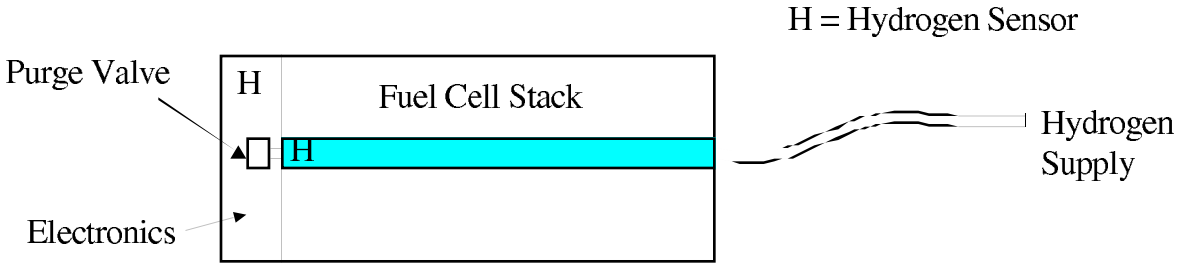

Figure 5 — Integration of Hydrogen Sensors into the System.

Many potential applications for the air-breather will require some level of remote status monitoring and operability or safety assurance. In addition, the buildup of inerts may be more challenging with some hydrogen sources or stack configurations. Hydrogen sensors may be advantageous in these cases. The parent company of Enable FCC, DCH Technology, has licensed and successfully commercialized state-of-the-art hydrogen sensor technologies including the Robust Hydrogen Sensor (RHS), from Sandia National Laboratories. These technologies are being integrated into the fuel cell system as depicted in Figure 5. One sensor is located within the stack to detect inert build-up, and would then trigger a brief purge. A second sensor is installed for safety and to detect leaks or excess build-up from the purges. The compact control electronics and the miniature purge valve are cleanly incorporated onto one end of the stack.

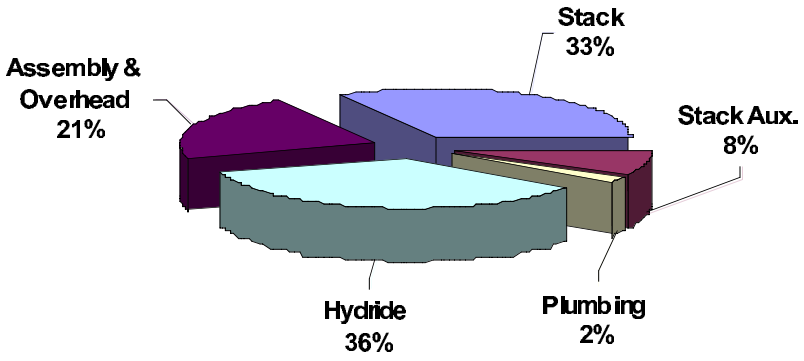

Figure 6 — System Component Costs (from Enable FCC)

As anticipated, a major issue coming into the forefront is hydrogen storage. In order to realize the energy density potential of the system, the metal or chemical hydrides need to be packaged particularly effectively. An overly complex or peripheral-burdened system would not be viable for portable power applications. Ideally, the fuel would be available in a cartridge that could be returned and recycled, or if it must be disposed (say, on foreign travel), it should not be an overly expensive loss. The economics element of the fuel supply issue is illustrated in Figure 6. As shown, the hydride storage system for this 4 W, 10 h system costs at least as much as the fuel cell, even though the latter involves numerous costly and special order components that have not yet had the benefit of high production levels to lower prices. While hydride production levels are not particularly enormous either, the business does have fairly large and established markets (e.g., Ni-metal hydride batteries). Costs for the hydride also may not be expected to decrease much further considering that the system is not particularly parts intensive, especially compared to the fuel cell. How the hydrogen is stored and supplied will naturally depend upon the application, but the overall system (storage + fuel cell) needs to be integrated and optimized. Portable power possibly provides some unique opportunities as to how this can be accomplished that would not be practicable on larger scale systems.

Conclusions

The air-breather has been shown to be an effective and versatile design over a wide range of sizes and packaging possibilities. Designs, understanding of the mechanics, and performances all continue to evolve. Although a number of aspects can be still further improved, the air-breather provides the durability and reliability necessary to become a commercial product and has demonstrated the performance and utility necessary to provide a successful fuel cell product. On the other hand, the complete system is still wanting, and the missing element is a cost-effective fuel storage system and its integration with the fuel cell.

Future Work

We plan to continue collaborating with Enable FCC in further evolving air-breather technology. As the fundamentals and optimal designs become better understood and more functional, opportunities arise to implement newer ideas and approaches that will bring the air-breather to the next technical levels. Already, Enable is pursuing new directions that can be particularly advantageous in many applications.

Since the interest in power supplies for personal electronics is particularly strong, more emphasis will be spent on the watt-level air-breathers. Because of the high surface area to volume ratios inherent in small objects, it should be possible to attain relatively high power densities and correspondingly develop some compelling devices.

As the air-breather design and understanding continue to evolve, additional issues are becoming more pressing. Paramount of these is the remainder of the overall system, namely the fuel storage and supply subsystem. The extent to which portable power fuel cells can be commercialized will be contingent on the safety, energy density and user-compatibility of the overall system, and we perceive that the weak link now is the fuel subsystem. Substantial progress has been accomplished with the fuel cell side of the system but now we believe that the emphasis also needs to encompass the fuel issues. Consequently, increased attention will be directed toward the hydrogen supply for the fuel cells. In this new aspect of the portable fuel cell effort, we intend to collaborate with Enable FCC and others to help develop and demonstrate portable storage technologies. Some of the challenges and opportunities inherent in a portable unit for commercial applications are very different than conventional storage requirements. As such, fairly conventional chemical hydrides that are not particularly attractive for large scale applications are possibly advantageous for portable systems. Thus, we are not trying to develop new chemistries so much as effectively and inexpensively adapt existing approaches and repackage them for portable power.

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