

ALKALINE FUEL CELL TECHNOLOGY FOR MITIGATING HYDROGEN GENERATED BY Mg/Fe BASED CHEMICAL HEATERS

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ABSTRACT

The Unitized Group Ration – Express (UGR-E) is a disposable, compact, self-contained module that provides a complete, hot meal for 18 warfighters. The UGR-E contains four shelf-stable polymeric food trays that are coupled to four magnesium based chemical heaters. With the pull of a tab, the food is heated within 45 minutes. Unfortunately, upon activation, the magnesium based heaters release a hydrogen gas by-product. Given that 400 g of heater material is needed for the UGR-E, the amount of released hydrogen gas (approximately 11 ft³) is formidable and could pose a safety risk if the lower explosive limit is exceeded. To address this problem, a lightweight, affordable, and disposable alkaline fuel cell (AFC) has been developed based on a flexible micro-tubular design. With this approach, the released hydrogen gas is consumed within the fuel cell to produce electricity and heat that may be used to further heat the UGR-E.

INTRODUCTION

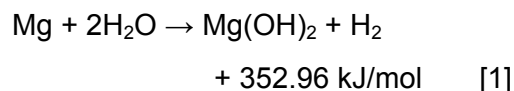
Chemical based heaters used by the military for Meals Ready-to-Eat rations release hydrogen gas upon activation. In larger rations that serve groups as opposed to individuals such as the Remote Unit Self Heating Meal (RUSHM) ration or Unitized Group Ration – Express (UGR-E), the released hydrogen gas is formidable and could pose a safety risk by detonating if the lower explosion level is exceeded. Consequently, it is desired to capture and use this hydrogen gas as opposed to venting it to

the surroundings. A photograph of a RUSHM unit is shown in Figure 1 after being activated with water that shows steam and hydrogen gas being released. In addition to mitigating the safety risk of exploding hydrogen gas, it is also desired to use this energy in a constructive manner to further heat the ration, allowing for longer heating periods or in helping to reduce the quantity of stored chemical reactants in the flameless ration heater (FRH).



Figure 1. Activated RUSHM with steam and hydrogen gas evolution

The flameless ration heaters are activated by introducing water into the heater pouch that starts to release heat, steam, and hydrogen after approximately one minute. Hydrogen gas is a reaction by-product of magnesium and water according to:



Given that 400 g of the magnesium heater material is needed for the UGR-E, the amount of hydrogen gas released during the 45 minute evolution period is over 11 ft³ at standard conditions. This is a formidable quantity and could pose a safety risk if the lower explosive limit is exceeded. In addition to mitigating this safety risk, it is also desired to use this energy (320 BTU/ft³ H₂) in the form of either heat or electricity as opposed to venting it to the ambient environment.

To address this problem, MicroCell Technologies, LLC conducted a Phase I SBIR program with the US Army Natick Soldier Center to develop and demonstrate a method for reacting all of the hydrogen gas released from the chemical based heater. This approach is based on using a micro-tubular alkaline fuel cell as a flexible heater cord. Hydrogen gas enters the interior of the tubular fuel cell while ambient air reacts on the external surface to produce water and electricity. The generated electricity may be passed through a resistive heater such as nickel-chromium that is wrapped around the cathode to serve as a dual functioning electrode and heater. In this manner, heat is generated along the length of the tubular fuel cell. This heater cord may be inserted into the flameless ration heater or snaked around the food packages to provide localized heating. Alternatively, the generated electricity may be extracted from the ration and used to conduct some type of useful work such as powering electrical conveyances or in recharging batteries that the soldiers may have.

APPROACH

The design of the alkaline fuel cell heater cord, FCord™, packages an alkaline fuel cell into a tubular architecture. As an example, a long, thin diameter (~ 10 mil) Ni wire is coiled to an approximate diameter of 0.1 inches in a helical manner as shown in Figure 2. This wire serves, by itself or with an additional coated catalyst, as the anode catalyst to react the hydrogen gas and as the current collector to extract electrons from the electrode reaction.

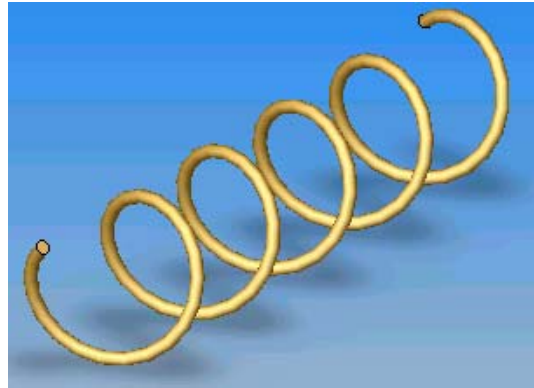


Figure 2. Helical nickel anode electrode and current collector

A thin 1 mil thick polypropylene separator or comparable separator material is wrapped around the Ni wire and sealed on one end by crimping or placing an end-cap at the end of the tube as shown in Figure 3. The opposing end of the tube is open to allow hydrogen gas to be introduced into the interior of the tube. A manifold fitting that connects the FCord™ to the RUSHM hydrogen supply is used to mate these two components together. This separator-wrapped anode is then coated and dried with KOH to form a dry film within the pores and surfaces of the separator matrix.

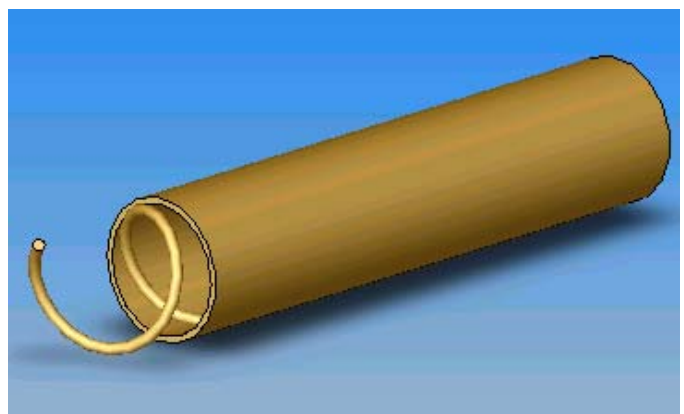


Figure 3. KOH imbedded separator matrix surrounding the anode

A Ni:Cr wire is then wrapped around this matrix to serve, by itself or with an additional coated catalyst, as the oxygen reduction electrode, the current collector, and

the resistive heater as shown in Figure 4. This cathode Ni:Cr wire is connected to the anode Ni wire to complete the electrical circuit: electrons flow from the anode to the cathode via these wires while ions flow from the cathode to the anode through the KOH electrolyte. We thus have made a flexible and tubular fuel cell that is activated once the electrolyte is moistened and hydrogen is introduced into the interior of the tube. A pictorially representation of the flexible tubular AFC heater cord is shown in Figure 5 with an end fitting on one side to connect to the evolved hydrogen gas from the FRH unit.

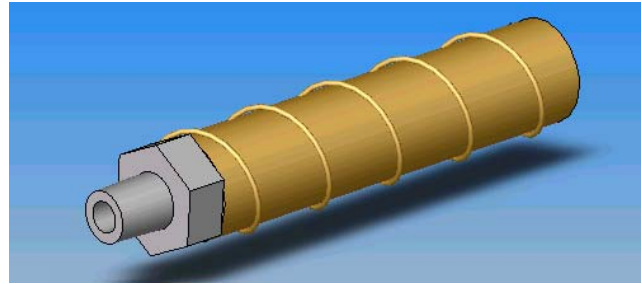
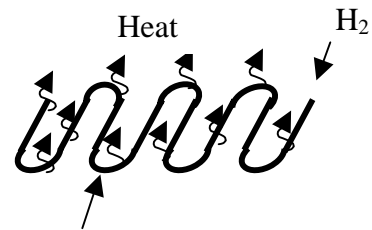


Figure 5. Pictorially representation of the flexible AFC heater cord, FCord™

Once the FCord™ is activated, the electrochemical reactions will occur with the electrons flowing to the resistive heater that surrounds the tubular cord. This Ni:Cr (nichrome) wire will heat up and provide heat along the entire length of the FCord™ assembly as shown in Figure 6. Since the overall diameter of the FCord™ is small at approximately 0.11" and consists of pliable wires and cloth, the FCord™ may be bent, flexed, and snaked around an object to heat it up in select locations. Thus, the FCord™ could be looped around the FRH itself adding heat to this component or the FCord™ could be applied to other locations on the food package such as the top or selectively on one side or region. Alternatively, the FCord™ could be extracted outside from the RUSHM and used to heat other items such as water, equipment, personnel, etc.



Micro-Tubular AFC

Figure 6. FCord™ schematic in operation releasing heat

The use of a micro-tubular AFC as a flexible heater cord is a novel approach for mitigating hydrogen released from the flameless ration heaters. Alkaline fuel cells are most commonly known for their present use onboard the Space Shuttles where they react hydrogen and oxygen to produce electricity and water for the astronauts. This space application has been very successful but costly. Extensions of the alkaline fuel cell to terrestrial applications have not seen as much success due to electrolyte leakage, corrosion, and carbonate buildup in the KOH electrolyte. Although AFC technology has several perceived "drawbacks", our unique application found these to be an advantage:

- Longevity is not required, thus, expensive electrodes (Pt, Au) have been replaced with Ni and NiCr wire.
- The electrolyte can be stored dry and then wetted upon heater activation. This

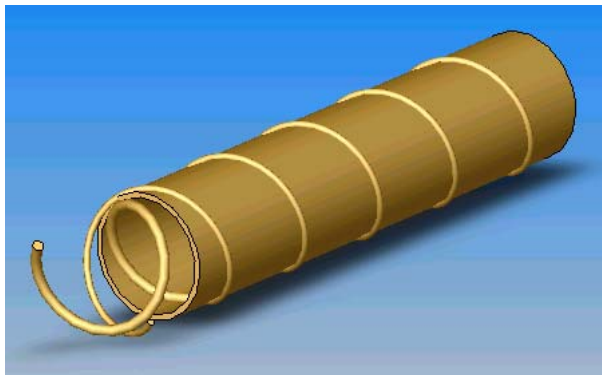


Figure 4. Cathode electrode, current collector, and resistive heater wrapped around the tubular AFC

eliminates electrolyte leakage and extends the shelf life indefinitely.

- Only operating for 45 minutes, CO₂ adsorption is negligible into the KOH electrolyte that could precipitate K₂CO₃ lowering the ionic conductivity.¹
- Inexpensive electrode and separator materials may be used since the device only has to work for a limited time at a fixed operating point.

SEPARATOR DEVELOPMENT

In all electrochemical systems an electrolyte is needed to conduct ions from one electrode to the other. This electrolyte is typically in the form of a liquid that either freely flows between the electrodes or that is immobilized in a separator. The separator is designed to keep the electrodes apart preventing electrical short-circuiting, keeps the anode and cathode reactants apart so they don't mix, and holds the electrolyte that completes the circuit by allowing ions to access each electrode.

The alkaline fuel cell uses a solution of potassium hydroxide (KOH) to allow hydroxide ions to migrate between the electrodes. A typical concentration is 30% (wt.) that gives one of the highest values of ionic conductivity for this electrolyte. For the FCord™, this electrolyte needs to be present between the electrodes in a separator that is dried out before storage to prevent the electrolyte from weeping. Upon activation of the chemical heater with water, the water present in the system can wet up the dried-out electrolyte/separator forming an ionically conductive pathway that completes the electrical circuit for the FCord™. Thus, necessary requirements for the separator are:

- 1) Can be wetted with electrolyte and dried out to "turn it off" until activated
- 2) Can be activated with water quickly giving adequate ionic conductivity

- 3) Does not allow hydrogen gas to permeate through it
- 4) Is thin enough to minimize the ohmic drop through the separator
- 5) Can be assembled into a tubular form

To demonstrate this approach, we examined a few different types of separators. One is a fiberglass mat consisting of woven fiberglass strands and the other material is 1 mil thick polypropylene sheet available from Celgard. Within the polypropylene material, we also have various types that have low or high porosity and surfactant and non-surfactant coatings. This polypropylene separator material is used in electrochemical systems in particular for batteries including lithium ion, nickel-zinc, and alkaline systems.

Separator Permeability

In order to assess hydrogen gas cross-over through these separators, we applied a differential pressure of hydrogen gas across the separator and examined if bubbles would permeate the membrane. For both fiberglass and polypropylene separators, gas permeation was observed when the separators were dried but not observed when the separators were wetted with KOH up to a differential pressure of 2 psid for fiberglass and 20 psid for polypropylene. The 20 psid measurement for polypropylene was where the experiment stopped and not where the separator started permeating hydrogen so it is possible that even higher differential pressures may be used with wetted polypropylene.

Since the intended application of the alkaline fuel cell in the RUSHM is at ambient pressure, both separator types will be feasible because they have negligible hydrogen permeation when wetted and are easily activated with water to become ionically conductive.

Separator Activation

A test apparatus was developed that allowed us to measure the DC resistivity in

the separators measured in the x-y plane and in the z-direction. This apparatus allows us to assess the conductivity of the separators in the pristine, wetted, dried-out, and re-wetted states.

We applied this method to fiberglass and polypropylene 2401, 3401, and 3501 saturated in 30% KOH. We also dried out these samples and re-wetted them with water and measured the resistivity again. This helps to assess how the separators will perform once activated with water in the RUSHM. When re-wetting the samples with water, a couple of drops of water were dripped onto the separator where it was observed that the water quickly spread out over the surface of the separator.

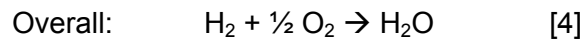
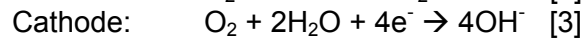
The 3401 polypropylene separator has a 37% porosity and contains a surfactant while the 3501 separator also contains this surfactant but has a higher porosity of 55%.

Figure 7 shows the results for the fiberglass and polypropylene 3401 and 3501 samples. Upon re-wetting the separators with water and measuring the resistivity, both polypropylene separators showed increased resistance with the lower porosity sample (#3401) showing a higher resistance than the higher porosity resistance.

The fiberglass mat showed very little difference in the resistance when re-wetted with water, but since it is much thicker than the 1-mil thick polypropylene sheet the overall resistance of fiberglass (16 ohms) is similar to that of the #3501 polypropylene sheet (13 ohms). Thus, either the polypropylene 3501 separator or a thin fiberglass mat may be used as the separator that readily wets up with KOH, may be dried out and re-wetted with water to give an adequate conductivity. Furthermore, both of these separator choices will not significantly permeate hydrogen once the separator is wetted with water preventing hydrogen from escaping the FCord™ and leaking into the RUSHM or ambient environment.

ELECTRODE DEVELOPMENT

The anode and cathode electrodes serve to oxidize the hydrogen and reduce the oxygen in air according to:



For these reactions to occur, a suitable catalyst is necessary to speed up the reaction rate. Typically, precious metal catalysts are

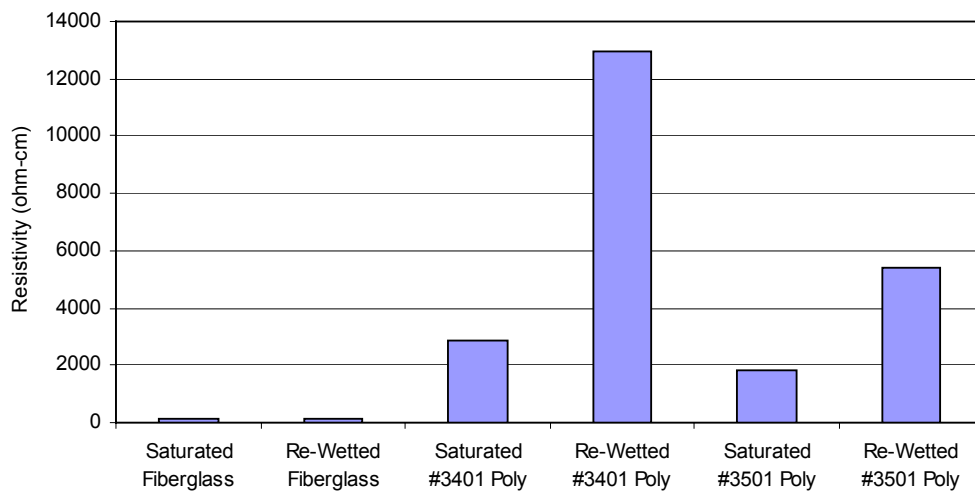


Figure 7. Comparison of resistivities of AFC separator materials in 30% KOH

used in fuel cells including platinum and gold to maximize the lifetime and increase the performance. However, for the intended application that only needs a 45 minute lifetime, we don't have to be concerned with long life performance, just sufficient activity and low cost. To this end, we set out to use inexpensive catalyst materials including nickel wire as the anode base and a nickel-chromium wire as the cathode base.

Improved electrodes may also be fabricated using the nickel wire anode and nickel-chromium cathode with Raney nickel and MnO_2 based catalyst, respectively. One of the approaches we took was to make an electrode that has a distinct region for a current collector mesh with good gas-distribution properties and a distinct region for catalytic reactivity. Thus, we fabricated a wet-proofed current collector mesh to serve as a gas-diffusion layer and fabricated a catalyst reaction layer to serve as the zone for reactions to occur. In this manner, the gas-diffusion layer is oriented such that hydrogen or air can readily flow into it and the catalyst layer is located next to the separator.

For the anode, a Raney nickel electrode was made by mixing an alloy of Ni:Al (50:50 wt%) in 30% KOH to dissolve the aluminum.^{2,3} This mixture was then drained and rinsed in water to remove the aluminum and salts resulting in a fine black powder. This powder was heated at around 40 °C in air to passivate it since it is pyrophoric. This was then processed with other electrode constituents to form an anode reaction layer. The anode needs to be activated by applying a small reductive current to convert the passivated nickel into a proton-adsorbed surface. This was done by placing the anode material in a 30% KOH solution and applying a reductive current of approximately 4 mA/cm² for a few hours.

For the cathode, MnO_2 was mixed with various electrode constituents and formed into a cathode reaction layer on the nickel or nickel-chromium current collector wire.⁴

An initial evaluation was made on a tubular alkaline fuel cell that was constructed using a nickel wire anode and a NiCr wire cathode with a polypropylene separator. A length of 3.25 inches was fabricated for this tubular fuel cell. This cell had hydrogen gas passed through the internal region with ambient air migrating to the external surface. Figure 8 shows the polarization results for this test operating at ambient conditions.

By optimizing the porous gas-diffusion electrodes with hydrophilic and hydrophobic compounds, decreasing the ohmic losses via improved electrolyte distribution, and increasing the kinetic activity by operating the cell at higher temperatures of 80 – 100 °C, we can increase the operational current density of the AFC to 1-2 A/cm².^{5,6}

In terms of assessing the size of the alkaline fuel cell reactor/heater, we can determine the required active area for reacting 11.3 ft³ of hydrogen in 30 minutes. This is shown in Figure 9 with the best measured alkaline fuel cell data obtained to date. The theoretical curve between the current density (hydrogen consumption rate) and the active area size as governed by Faraday's Law is also shown in Figure 8. By continuing to increase the current density and packaging the AFC into a compact tubular form we can continue minimizing the overall size and, hence, cost as also shown in Figure 9. Furthermore, we have not factored into this yet the possibility of the waste heat and the heat generated by the AFC heater in the nichrome wire for providing further heat to the RUSHM that would lessen the amount of the chemical heater material upfront further reducing the required size of the AFC reactor/heater.

Based on a projected operational current density of 2 A/cm², the required active surface area is on the order of 1000 cm². With this AFC size, it would weigh only 100 – 200g, a small fraction of the 30lb UGR-E unit. Based on these weights, the AFC will provide almost 20 W/g of weight added, in the form of heat or power. In the form of heat, this

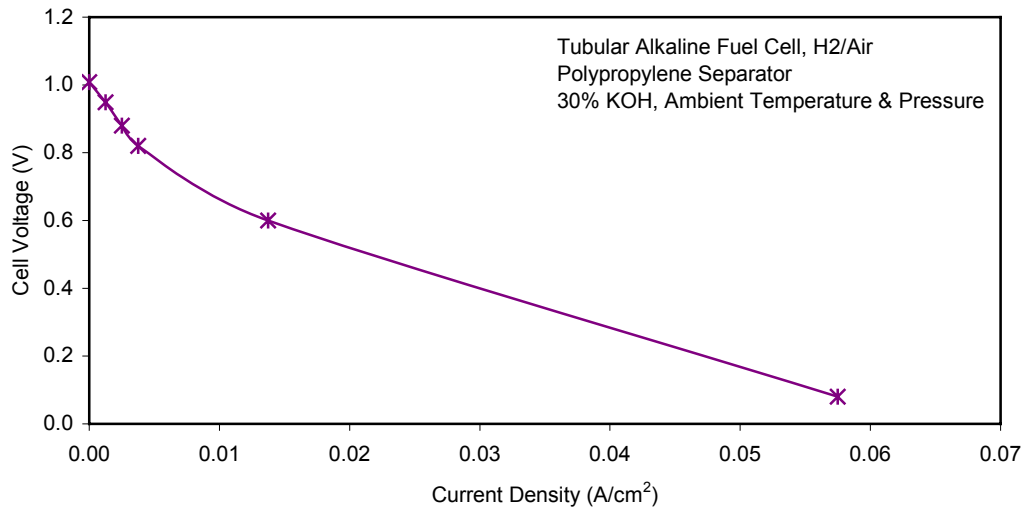


Figure 8. Tubular alkaline fuel cell performance

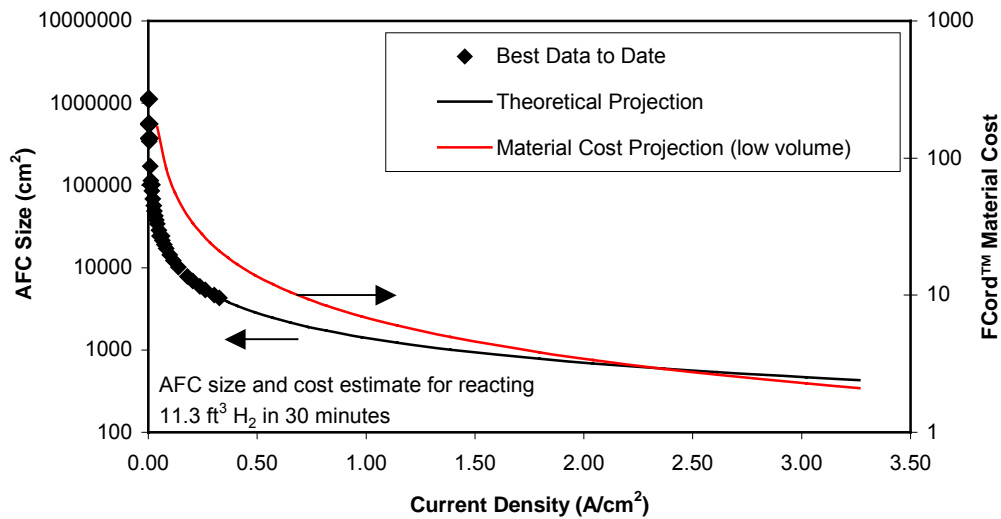


Figure 9. Size reduction of the AFC reactor/heater with increasing current density

equates to almost 20% of the UGR-E heat output, leading to a reduction in the mass of magnesium heater required. More importantly, the hazard created by the hydrogen has been treated, while still yielding over 300 W-hours of power from the UGR-E; power that will ultimately benefit the Soldier.

SUMMARY

Our work to date on the FCord™ technology has demonstrated the proof-of-concept of using a tubular alkaline fuel cell to react the hydrogen gas from the RUSHM unit. We have

- 1) Shown that these tubular fuel cells may be fabricated
- 2) Shown that a nichrome wire may be used as dual functioning cathode and heater

- 3) Demonstrated that the FCord™ electrolyte may be dried out (to give a long storage life) and quickly activated with water on a time scale much less than the chemical heater
- 4) Demonstrated methods and fabrication approaches for the electrodes along with identifying important parameters in the electrode that govern fuel cell performance
- 5) Assessed low volume material costs of the FCord™ for reacting 11.3 ft³ of hydrogen in 45 minutes giving cost values less than \$10/RUSHM unit, and
- 6) Conducted preliminary sizing and integration of the FCord™ in the RUSHM indicating that the tubular alkaline fuel cell will fit readily into the chemical heater trays.

We have identified various electrode constituents that may be used to help improve the electrochemical performance. In particular, we have shown that low-cost, non-noble metal catalysts may be used with the alkaline fuel cell to keep the cost low. For the anode, nickel along with Raney Nickel catalyst may be used to oxidize hydrogen and for the cathode, nickel-chromium along with manganese oxide may be used to reduce air. We also examined a number of

oxygen in the hydrophilic and hydrophobic constituents and found that they greatly influence the electrochemical performance.

A number of separator materials were evaluated including fiberglass and polypropylene. We examined methods for wetting and drying the KOH electrolyte into the pores of these materials. We found that we could easily and quickly re-wet the dried electrolytes by a little moisture within a couple of seconds, a time period much shorter than that for activating the chemical heater in the RUSHM. We found that 1 mil thick polypropylene sheet served as a good separator material that is low cost and amenable to being rolled into a tubular alkaline fuel cell.

We examined a number of tubular alkaline fuel cells showing that the fundamental process works for mitigating hydrogen. Continued optimization of the structure, electrodes, and electrolyte distribution throughout the cell will allow us to achieve high power density flexible cells. A photograph of an 85 mil diameter, 24" long tubular alkaline fuel cell prototype is shown in Figure 10 that when operated at 2 A/cm² will produce 40 watts of power and weigh only 2.1 g and occupy 2.3 cc.



Figure 10. Photograph of a 40 W tubular AFC prototype (patent pending)

ACKNOWLEDGEMENT

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