

SPIRAL-WOUND PEM FUEL CELLS FOR PORTABLE APPLICATIONS

T.J. Blakley, K.D. Jayne, and M.C. Kimble

MicroCell Technologies, LLC, 410 Great Rd, C-2, Littleton, MA 01460

Lighter weight and compact fuel cells are desired for low power levels less than 50 watts. Often, PEM fuel cells in this category are smaller versions of the larger planar fuel cells maintaining similar components. However, for low power level systems, the currents are often on the order of a few amps and thus do not require bipolar plates, but can instead rely on edge-tab current collection. A cylindrically designed PEM fuel cell can help reduce the stack mass and volume for small portable systems. A membrane and electrode assembly envelope is wrapped around a mandrel core for supplying hydrogen while ambient air diffuses from the ends. Metallic screen current collectors and carbon-free electrocatalysts allow the cell to operate in both fuel cell and electrolyzer modes. A benefit of this reversible cylindrical fuel cell is that it minimizes the number of components thus helping to maximize the energy density for portable power applications.

Compact and Portable Fuel Cells

Electronic devices such as cell phones, computers, and cordless power tools have made portable power a mainstay in the consumer, commercial and military sectors of our economy. Presently, portable power is dominated by the battery. While increases in power density have been made in battery performance over the last three decades, the marketplace demands further increases in energy density and capacity, with the focus being on rechargeable batteries. Typically, though, a good state-of-the-art rechargeable lithium ion battery will have an energy capacity on the order of 150-200 W-hr/kg. Energy capacities that far exceed this level are desired for many portable power applications.

Historically, traditional planar fuel cell designs advocate operating at high current densities in order to minimize the fuel cell capital cost and mass. For stationary and automotive fuel cell systems, operating at low current densities and high cell voltages can lead to platinum migration into the membrane lessening the stack lifetime for these applications. However, for a portable power application, long operating lifetimes are not the driver, but compactness, weight, cost, and ease of use are. One benefit of operating a portable fuel cell at high voltage efficiencies is that less waste heat is generated in the fuel cell reducing cooling demands. Another benefit is that less fuel needs to be stored improving volumetric and gravimetric energy capacities of the complete energy storage system. Furthermore, operating the fuel cell at high voltage efficiencies lowers the current density of the stack allowing dry reactant gases to be used. Typically, humidified gases are used since high current densities are often sought. However, at low current densities, the water produced on the cathode is capable of diffusing through the membrane to offset the electro-osmotic drag of water with protons migrating from the anode to the cathode. Consequently, the membrane maintains an adequate hydration state

with a concomitant sufficient protonic conductivity to sustain the electrochemical reactions.

Removing bipolar plates and end-plates from our spirally-wound fuel cell gives us a lightweight and compact design. Increasing the active area to generate more current has a marginal impact on the mass and volume due to the spiral configuration. Consequently, we can operate the cell at high cell voltages to minimize or eliminate balance of plant components. The low current density ($< 40 \text{ mA/cm}^2$) at these high cell voltages ($> 0.9 \text{ V}$) is easily sustained with ambient air diffusion to the cathode since it operates well below mass-transfer limited currents.

Design Approach

A cylindrical PEM fuel cell can be fabricated by first developing a membrane and electrode assembly “envelope” instead of a flat MEA sheet. The process starts by chemically catalyzing two Nafion sheets with a platinum catalyst on both sides of each sheet. These two sheets are laid over each other where three of the sides are thermally bonded to form a membrane and electrode assembly envelope. In this manner, no gaskets or seals are used in the process. With the MEA envelope structure, the hydrogen electrodes are located inside the envelope facing each while the oxygen electrodes are located on the outer surfaces. This MEA envelope forms a single cell since upon rolling the MEA, the exterior cathode surfaces contact one another. Unrolled dimensions of the MEA envelope have ranged from 1” to 6” long in the axial direction and 2” to 10” long in the radial direction. To the interior of the MEA envelope we can insert a gas-diffusion media such as a Teflonated carbon cloth that is carbon coated on both sides to improve electrical conductivity with the catalyzed membrane surfaces. A current collector wire is inserted into this envelope to transfer electrons along with a small diameter capillary tube that connects to the hydrogen storage source. In this manner, hydrogen gas is readily distributed throughout the envelope interior once the MEA is wrapped around a central core.

In the next step of the manufacturing process, a central core consisting of an open tube is used to serve as a hydrogen manifold where the MEA envelope is wrapped around. This central core diameter can range from 0.125” to 0.25” in diameter and consist of either polypropylene or Teflon as representative materials. Larger diameter central cores may be used to hold multiple MEA envelopes that can be used to increase voltage in the spirally-wound stack beyond one volt. The MEA envelope is inserted into an incision in the central core with the open seam of the envelope located inside the core and the current collector and capillary flow tube extracted from the inside of the central core. An epoxy resin is applied inside this central core thus sealing only the opening of the MEA envelope. In this manner, the open seam of the MEA envelope is sealed with the current collector wire and hydrogen flow tube extracted outside of the epoxy-filled central core. By introducing hydrogen into the capillary tube, hydrogen gas readily flows into the MEA envelope and even inflates the envelope if the pressure is sufficient. Electrical contact inside the envelope is made via the current collector wire that protrudes from the edge of the epoxy-filled central core.

To the external oxygen electrodes we place either a carbon cloth or metallic screen over each electrode along with a single Teflon mesh located on top of one of the gas-diffusion/current collector screens. The metallic screens serve as current collectors that contact the catalyzed membrane surfaces while the Teflon mesh provides air gaps for lateral air diffusion or convection into the cell once the MEA is wrapped into a cylindrical configuration. Teflon meshes on the order of 15 mils thick with approximately 18 openings/inch have been used for this application. A single metallic screen and air flow diffuser may also be used. The material choice for the oxygen side gas-diffusion and current collector assembly will depend on whether the cell is designed to operate in the fuel cell only or both fuel cell and electrolyzer modes. For a cell designed to operate only in the fuel cell mode, we can place a carbon cloth gas-diffusion backing on both outer surfaces of the MEA envelope. For a cell designed to operate in both the fuel cell and electrolyzer modes, a better material is a platinized titanium or stainless steel screen that will not oxidize during the water electrolysis reaction.

To complete the spirally-wound cell, we wrap this assembly around the central core binding it with either tape or a label. During this wrapping process, radial compression is produced making suitable electrical and ionic contact between the interfaces. The use of tape to bind the cell eliminates the traditional stack end-plates while the use of current collector screens eliminates the traditional bipolar plates. Consequently, the cell is lighter in weight and volume. The small capillary tube from the interior anode region in the MEA envelope is inserted into a fitting that connects to a hydrogen source and the current collector leads for the hydrogen and oxygen electrodes are slightly extracted from the cell. A schematic of the spirally-wound fuel cell and electrolyzer is shown in Figure 1. With this cell, oxygen in air can diffuse via either side of the cell toward the middle while hydrogen is introduced via the capillary tube inside the MEA envelope. Since the MEA envelope is sealed, the hydrogen and oxygen remain separated allowing the electrochemical reactions to proceed in either fuel cell or electrolyzer operational modes.

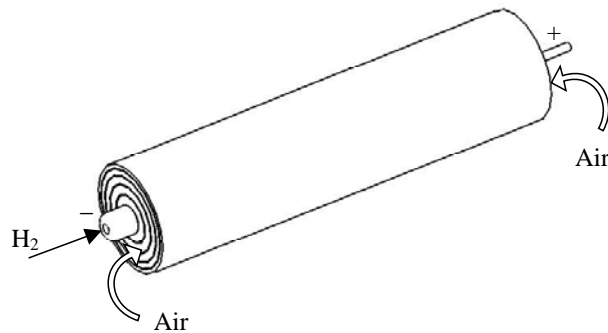


Figure 1. Schematic of a cylindrical PEM fuel cell (patent pending)

Membrane Catalyzed

Most fuel cell electrodes are based on a platinum/carbon catalyst where it is often applied on a gas-diffusion layer (GDL) or directly on the membrane. Using catalyzed GDL electrodes usually requires that they are thermally bonded to the membrane to

minimize interfacial contact losses in the MEA. Alternatively, direct membrane catalyzation places a thin (~ 10 microns) catalyst layer on the membrane to minimize interfacial contact resistance where an uncatalyzed GDL is placed up against the membrane.

For the spirally-wound fuel cell and electrolyzer, we want to catalyze each side of the membrane with distinct catalytic properties. Thus, the fuel cell anode side might contain a platinum catalyst with or without a carbon support whereas the fuel cell cathode side might contain a mixture of platinum and iridium oxide with the absence of carbon. To make a reversible electrode for the oxygen side of the fuel cell (cathode) and electrolyzer (anode), it is imperative to keep carbon out of the electrode and gas-diffusion layers since it will oxidize during electrolysis to carbon dioxide. Hence, we use different catalyzation methods for making hydrogen and oxygen electrodes for the reversible fuel cell and electrolyzer.

A number of investigators have examined using tetraammineplatinum(II) chloride, to directly catalyze ion-exchange membranes (1-3). We have used variations of this process in fabricating tubular fuel cell and electrolyzers and adapted it for producing the spirally-wound fuel cell (4-6). The general process immerses an ion-exchange membrane in a plating bath of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ to exchange proton groups in the ion-exchange membrane with platinum groups. This exchange process is dependent on the plating bath concentration, temperature, time, solution agitation, and membrane volume. Following this initial ion-exchange process, the membrane is immersed in a reducing solution of sodium borohydride, NaBH_4 , to chemically reduce the platinum ions to metallic platinum in the membrane and on the membrane surface. This reduction process is also dependent on the sodium borohydride concentration, temperature, time, solution agitation, and membrane volume. SEM analysis of membranes catalyzed with this process show approximately 5 micron thick platinum films on the membrane surface with a 1-2 micron thick penetration into the membrane. No isolated platinum particles are observed within the membrane interior when optimal chemical catalyzation parameters are used. Figure 2 shows a representative cyclic voltammogram showing the largest platinum surface area occurring with a reductant concentration of 0.2M. In practice, we have found this direct membrane catalyzation method to give varying results in the fuel cell operational mode due to inconsistencies in the fabrication method. Thus, we conducted an experimental investigation of the readily identifiable variables in the catalyzation process as discussed above to optimize the electrochemical performance.

One of the important variables to assess with the direct membrane catalyzation process is the real surface area of the platinum catalyst that is available to participate in electrochemical reactions. Depositing more platinum on a membrane or in an electrode does not necessarily increase the quantity of available surface area since interior regions in the platinum film may be covered by subsequent platinum layers. Thus, in developing a high performing MEA we measured the electrochemically active surface area as an indicator of the catalytic capability of the MEA.

Using cyclic voltammetry (CV), the determination of the real surface area of bare Pt-electrodes is based on the formation of a hydrogen monolayer electrochemically adsorbed at the electrode surface. Integration of the peak areas during the cathodic sweep in the hydrogen deposition region of the CV may be used along with a value for the

known charge transfer per unit area, $210 \mu\text{C}/\text{cm}^2$, to calculate the real Pt-electrode surface area (7).

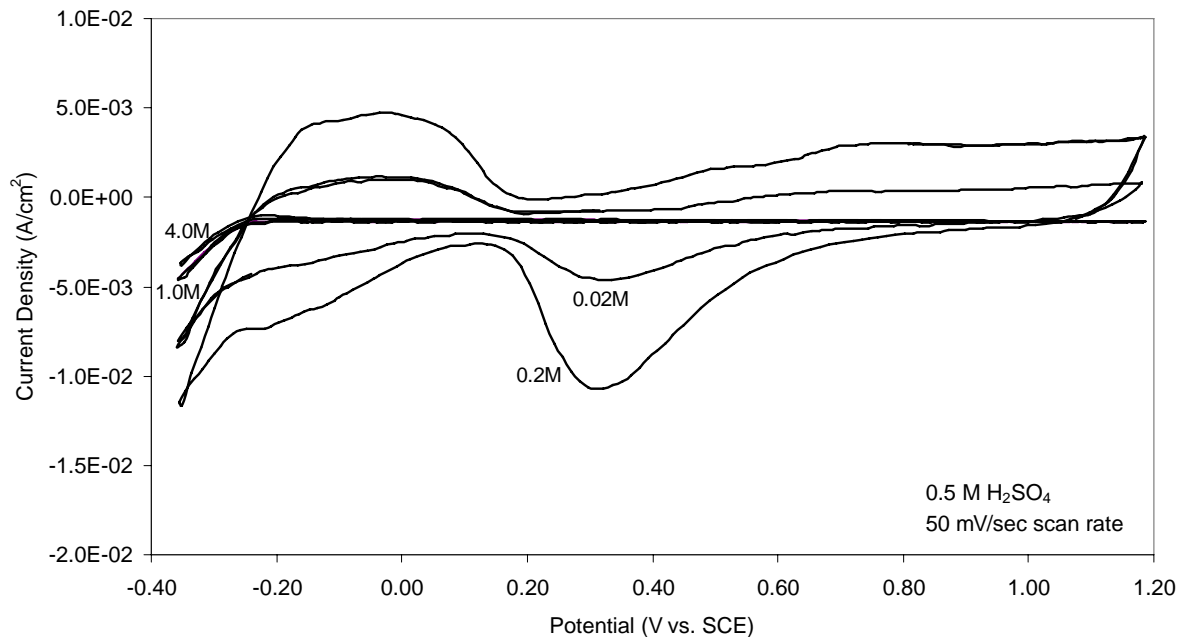


Figure 2. CV performance for MEAs catalyzed with varying reductant concentrations

From this catalyzation investigation, we showed that the membrane catalyzation process exhibited dosimetric behavior for both the initial platinum ion-exchange and the subsequent platinum reduction steps. Thus, the tetraammineplatinum chloride concentration and immersion time are related and should be approximately 113 mM-min. Similarly, for the reduction process, the platinum ion filled membrane should be exposed to a dosimetric exposure of 6.0 M-min of sodium borohydride. Using these dosimetric values, we obtained the highest platinum surface area within our study of $177 \text{ cm}^2 \text{ Pt}/\text{mg Pt}$ as determined by cyclic voltammetry. Repeated platinization cycles may be conducted to further increase the platinum loading and charge transfer capability, but at a higher cost due to the higher platinum loading. With this catalyzation method, equal catalyst loadings may be applied to opposing surfaces of the membrane by subjecting both membrane surfaces to the plating solutions. Alternatively, variable loadings may be applied to each side of the membrane by masking one side or subjecting the plating chemicals only to one side of the membrane. This method would allow more catalyst to be used for the cathode surfaces and less for the anode surfaces. Although not investigated, performance improvements could be possible by applying additional ionic conducting medium to the catalyzed surfaces to extend the reaction zone into the 3-dimensional region of the catalyzed film.

Two growth mechanisms for the catalyst surface area were observed with this platinization method. The first growth process is driven by platinum ion reduction to its metallic state as a result of dosimetric loadings and diffusion. The second growth mechanism appears to be due to catalytic hydrogen formation on the platinum particles from NaBH_4 that conditions the catalyst increasing the surface area. Using the same NaBH_4 concentration and reduction time, we varied the reductant temperature over a

series of membranes and measured significant differences in the membrane's surface area and charge transfer behavior. Since these MEAs were catalyzed with the same reductant concentration and duration, similar diffusion of the reductant inside the membrane would be expected. Since the reductant temperature strongly affected the resulting catalyst charge transfer and surface area, we infer that a kinetically controlled process is responsible for the platinum deposition and not one based on just chemical diffusion as suggested in the literature (3).

Cell Performance

One of the advantages of the spirally-wound fuel cell approach is that wrapping the MEA envelope around itself forces good electrical contact between the electrodes and current collector screens. This is shown in Figure 3 for an MEA envelope tested unwrapped and wrapped around the central core. As shown, improved performance was obtained in the wrapped cell due to better interfacial contact with the electrodes. In these tests, the hydrogen flow was dead-ended into the cell and ambient pressure and temperatures were used. The platinum loadings on the membranes varied in the 0.3 to 0.5 mg Pt/cm² range for these cells.

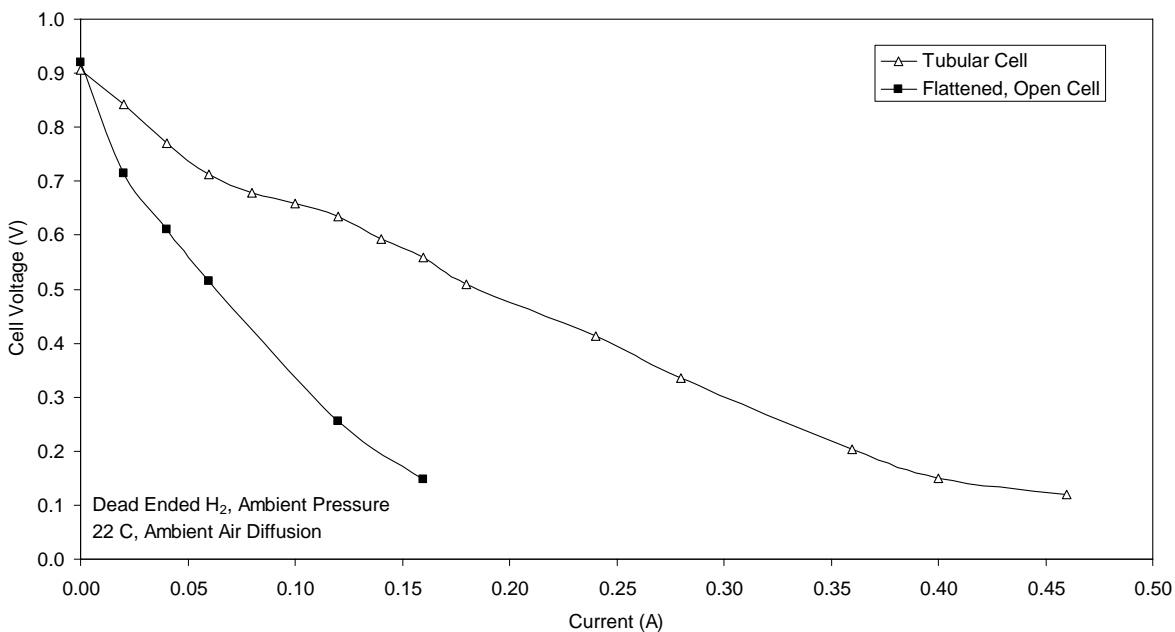


Figure 3. Flattened and wrapped MEA fuel cell performance

Most of our fuel cell development efforts center about ambient pressure and ambient to low temperature conditions since these operating conditions are more consumer acceptable. A higher operating temperature up to 56 °C was tested on our MEAs with dry gases under ambient pressure conditions showing improved performance up to 40 °C with a decline in polarization behavior at the 56 °C level as shown in Figure 4. This is most likely due to the membrane drying out with the dry reactants at 56 °C that lowers the ionic conductivity of the membrane. With a goal of operating the cell at 40 °C, our operation with dry reactant gases is satisfactory while still maintaining a user-friendly

energy storage system. Dry hydrogen gas dead-ended into the cell and ambient air diffusion to the cathode were used in these tests.

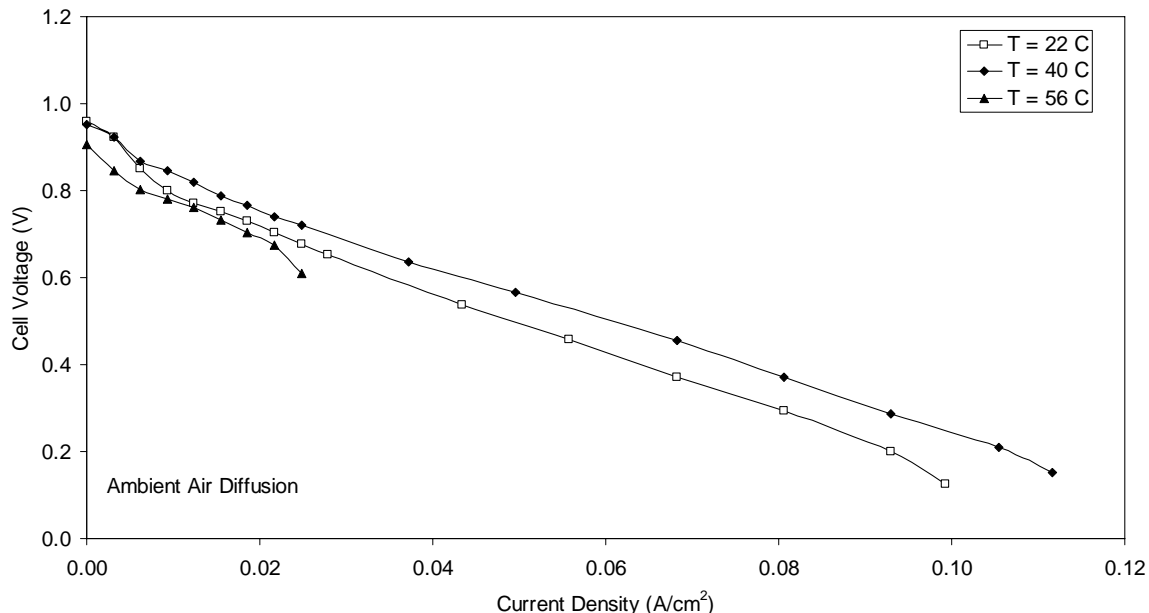


Figure 4. Temperature effects on fuel cell performance

One of the beneficial features of the platinization method used for fabricating the membrane envelope is that the outer platinized surface is electrochemically active and electronically conductive. This allows us to modify the external MEA envelope surface by electrodepositing improved catalysts onto the surface. For instance, the electrolysis of water is improved using ruthenium oxide or iridium oxide catalyst over that of platinum (8). Iridium oxide was electrochemically deposited using a similar method discussed by Baur (9). In this method, H_2IrCl_6 is dissolved in a basic solution and electrochemically deposited onto the outer surface of our platinized membrane envelope. Iridium oxide loadings of approximately 1 mg/cm^2 were targeted with this method.

This dual functioning spirally-wound fuel cell and electrolyzer was evaluated in both operational modes. We examined first the affects of forced ambient pressure and temperature air convection versus ambient air diffusion into the cell. Afterwards, the cell was evaluated in the electrolysis mode by immersing it in water to coat the outer electrodes. Ambient pressure and temperature conditions were used for the dry, dead-ended hydrogen flow and ambient air diffusion. Room temperature distilled water was used for the electrolyzer reactant.

The polarization results are shown in Figure 5 indicating no substantial difference in forced air versus ambient air diffusion into the cell when operated in the fuel cell mode. This is important to our system design approach where we rely on ambient air diffusion into the cell to avoid using air fans, blowers, or pumps in the system. This figure also demonstrates the spirally-wound cell operating in the electrolyzer mode in the same unit. Thus, the cylindrical design approach allows us to minimize components in the energy storage system to a reversible fuel cell/electrolyzer cartridge and a metal hydride storage cartridge.

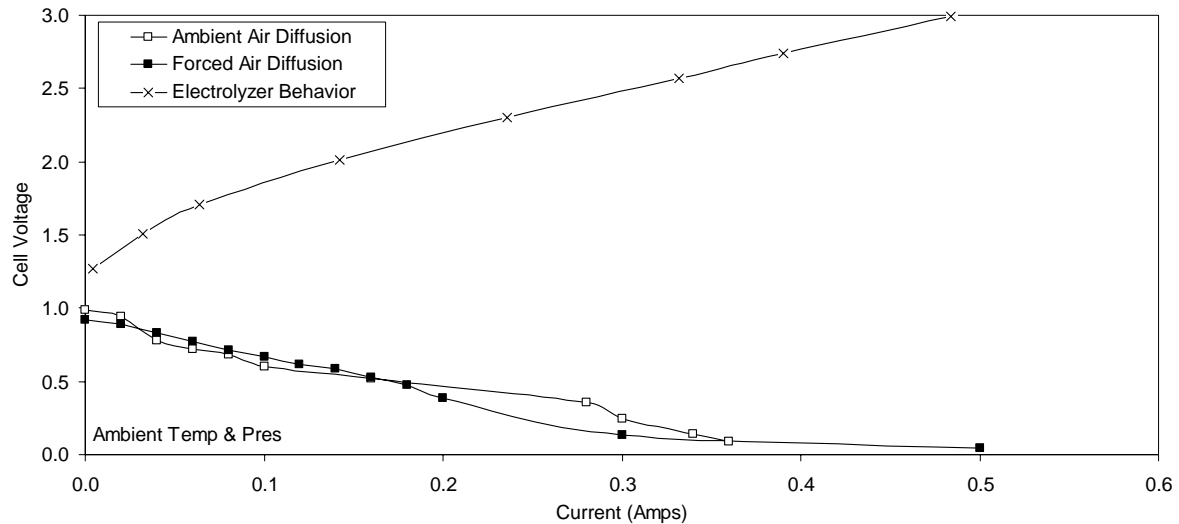


Figure 5. Reversible operation in a spirally-wound fuel cell

Energy Storage System

Our consumer energy storage system approach centers about using a single reversible fuel cell and electrolyzer module along with a metal hydride storage module. Alternatively, a chemical hydride storage unit may be used for a refillable energy storage system offering higher energy capacities. The fuel cell and fuel storage modules are designed to connect together in series to serve as the entire energy storage system. The approach specifically aims to replace, or supplement, batteries in normal consumer devices without requiring changes to the electronic devices. Using a single MEA envelope, cell voltages less than one volt are attainable that can be increased by connecting more cells in series as done with batteries. Alternatively, multiple MEA envelopes can be mounted in a single central core resembling a flag pole with multiple flags. Interconnecting anode and cathode layers accordingly, increased voltage in the cell may be attained when these MEA envelopes are wrapped around the central core. In order to keep the energy storage system simple and similar to a battery system with no moving components or control devices, we have strived to develop the system using practical operating conditions for pressure, temperature, and reactant gas quality.

This energy storage system design does not require external components such as heaters, humidifiers, pumps, fans, compressors, blowers, regulators, valves, etc. that most compact fuel cell power generators contain. By purposely designing our system to operate at lower temperatures, pressures, and with dry hydrogen and air reactants, we do produce lower power levels than what could be attained with more aggressive operating conditions; however, by removing these components we simplify the system to just two major components helping to minimize the overall mass, volume, and cost of the system while maximizing the reliability since there are few components.

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