

Short communication

Passive air management for cylindrical cartridge fuel cells

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Abstract

A novel air management system was developed to control diffusion for higher performance cylindrical fuel cells. A passive cylindrical fuel cell with expanded graphite diffusion media was constructed and operated with hydrogen. Very stable open circuit potential was obtained with this volume efficient self-sealing construction. Temperature differences on the surface and fuel outlet were determined. Modifications to the diffusion media and good contact between the components were necessary for higher performance and stable power output. Proposed design helps to realize “Replaceable Cartridge Fuel Cell” concept. The mathematical relationship between porosity of the structure and maximum current density was determined based on an assumed diffusion coefficient value with fixed porosity through the body and varying tortuosity through the thickness of the diffusion media. Assumptions favor cylindrical design approach over flat design for smaller, volume efficient construction.

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1. Introduction

Micro and small fuel cells are considered as future power sources for consumer electronics as battery chemistries progress slowly to provide higher energy densities [1–3]. Any contribution to higher efficiency fuel cell development will help this alternative technology to surpass battery energy densities. The most appropriate approach to reach higher efficiencies is to operate the fuel cell in passive mode for both fuel and oxidant.

Cylindrical fuel cell design is a weight and volume efficient alternative to flat design to achieve passive operation [4]. Cylindrical designs may eliminate the need for additional plates on the airside to hold the structure together. The surface of the cell in either approach is exposed to atmospheric air to allow diffusion and reaction at the catalyst surface. Any passive cell design operates in an air-limited mode of operation due to the slow kinetics of oxygen reduction. Since power consumption of electronic devices requires a substantial amount of oxygen to reach the reaction site, the design of the gas diffusion layer on the cathode site is one of the most important factors in achieving higher performance.

GRAFCELL[®] natural graphite gas diffusion layer technology, from GrafTech, defined here as a mass transfer layer (MTL) to cover multi-component aspects of the diffusion process, allows the design of diffusion media to increase limited current through engineering modifications. These modifications provide additional benefits to the fuel cell operation such as water management to prevent flooding and self-sealing. Natural graphite based expanded graphite is used in making GRAFCELL[®] MTLs a monolithic binderless structure that is flexible, conformable and highly electrically and thermally conductive. Graphite sheets that are manufactured by the continuous sheet-forming processes are made permeable by mechanical (perforation) and chemical (pore formers) means [5]. Fig. 1 shows an example of such structure created by perforating Grafoil[®] expanded graphite sheet with 2500 tips in.⁻² tool. A variety of parameters including thickness of the structure, location, and the number of the holes and size of the openings can be optimized in order to maximize fuel cell performance. In this paper, theoretical considerations for passive fuel cell operation and cylindrical fuel cell prototyping with GRAFCELL[®] material are discussed.

2. Experimental

In-house cylindrical flow field plates and mass transfer layers were assembled with a Nafion membrane to have 5 cm²-active

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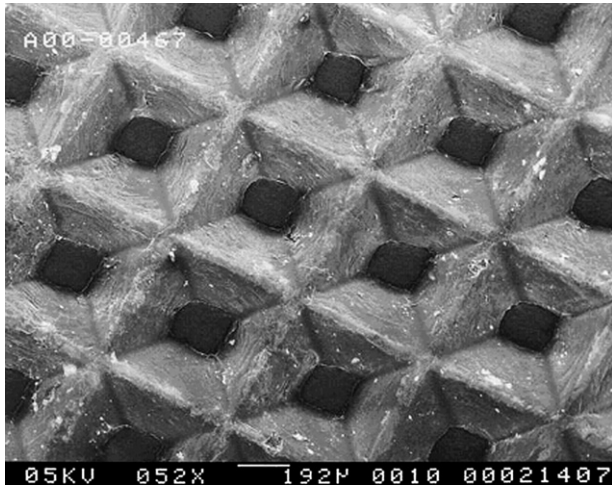


Fig. 1. SEM for expanded graphite mass transfer layer structure with 2500 tips in.^{-2} pattern.

area. Parallel flow field plate channels were machined on a graphite rod with 1 mm width and 1 mm depth. On the anode side, GRAFCELL[®] MTL was used with a carbon/PTFE coating and catalyst. Catalyst loading was 0.5 mg cm^{-2} Pt both on the anode and cathode. The cathode catalyst was placed on the membrane. The airside MTL had a hydrophobic micro porous layer (MPL) on the surface facing the catalyst and membrane. The whole system was placed inside a heat shrink tube and conditioned at 125°C for 5 min to provide compression and sealing to the structure. All testing was carried out at room temperature ($22\text{--}24^\circ\text{C}$), i.e. no external heating. A constant supply of hydrogen was used as it was generated from an electrolyzer.

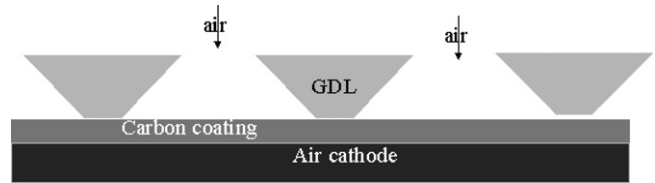


Fig. 3. Schematic of mass transfer layer, micro porous carbon coating and air cathode combination.

Some preliminary testing with methanol was also carried out. Atmospheric air was passively made available to the outside of the cell. The fuel cell was conditioned at open circuit voltage and was also polarized to various current densities before polarization data were taken at different current densities with 5–15 min open circuit rest between measurements.

3. Results

3.1. Cell construction

Fig. 2 shows a schematic of a single cell construction. The anode flow field plate (FFP) is either a tubular structure with permeability or a rod with machined channels on the surface. In the construction, layers of materials are placed on top of each other starting from the anode side. A GRAFCELL MTL with Pt catalyst was placed on the anode FFP. A tubular Nafion membrane was slide onto the anode MTL. Cathode catalyst was either placed on the membrane or on the MTL. The air cathode MTL provided exposure to the outside air (Fig. 3). A carbon coating on the surface of the MTL was necessary to ensure uniform distribution of air and water generated during opera-

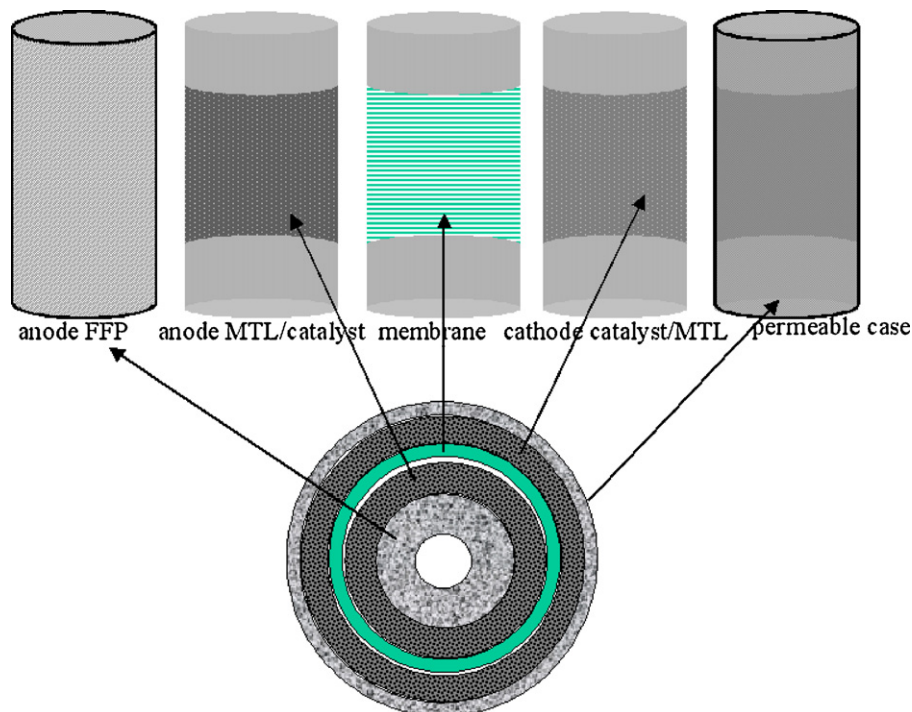


Fig. 2. Schematic of expanded graphite based cylindrical fuel cell construction representing assembly order.

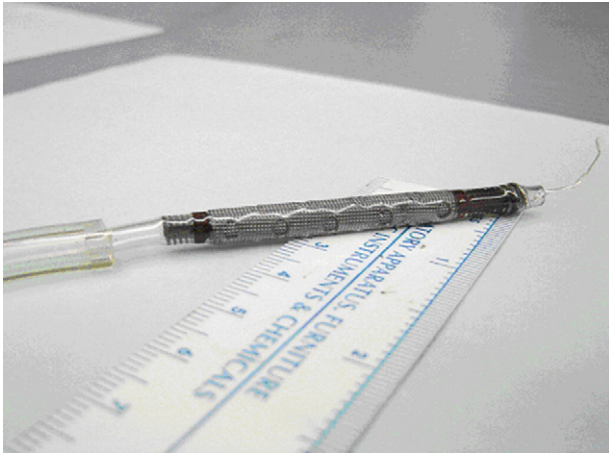


Fig. 4. Example of a prototype cylindrical fuel cell, 5 cm long and weighing about 1 g.

tion. The air access holes were perforated on the heat shrink tube that held the whole structure together without any other means. There was no need to use gaskets to seal the system. Edge of the assembly was seal proof through mass transfer layer where only active area was perforated, not the edges as seen in Fig. 2. This approach provided a fuel cell system that was volume and weight efficient, easier to fabricate, and cost effective. Battery shape factor allows this type of fuel cell design to be used as replaceable and refillable. GrafTech approach is very fuel flexible to allow fuel storage inside the cylinder for use on an as needed basis making “cartridge fuel cell” concept possible [6,7].

Fig. 4 shows one of the prototypes. Various cells were constructed in similar fashion with different types and sizes of anode flow field plates. This particular cell had about 5 mm outer diameter with the flow field plate having a 2 mm diameter. Rolling a 100–200 μm MTL on such a small diameter is only possible with a material that has a curvature diameter smaller than 2 mm. Similar construction could be done with carbon cloth material, but GRAFCELL[®] MTL can easily achieve this in a volume and weight efficient way without sacrificing performance.

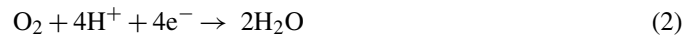
3.2. Passive air management

Since fuel cell performance is strongly determined by the airside diffusion media, optimum MTL design is necessary. As air diffuses to the surface of the cathode catalyst to react, generated water has to be removed from the reaction site together with nitrogen as air comes to the surface. However, this removal has to be optimum to prevent membrane dry out before it leads to lower cell performance. This multi-component cross diffusion challenge can be overcome by chemical and mechanical modification to the air diffusion media. More porous structures allow distribution of the oxygen mass fraction across the MTL resulting in a more active electrochemical reaction, which leads to an increase in the limiting current value. Large pore size allows a higher consumption of oxygen in the catalyst layer. However, distribution of pore sizes is needed for effective water management in the cathode structure.

In addition to the air diffusion impact, cell performance also depends on cell geometry. A one-dimensional diffusion equation can be solved for that impact on Cartesian or cylindrical coordinates. In Cartesian coordinates, the steady state diffusion equation takes the following form in the diffusion media:

$$\frac{d}{dx} \left[D_{eO_2} \frac{dC_{O_2}}{dx} \right] = 0 \quad (1)$$

with the boundary conditions [$x=0, C=C_b$; $x=L, C=C_o$]. In the above equation, D_{eO_2} is the effective diffusion coefficient of oxygen in $D_{eO_2} \Theta^r$ form where Θ represents porosity and τ represents tortuosity of the porous structure. C_{O_2} is the oxygen concentration in the diffusion media. Oxygen must diffuse through a stagnant nitrogen volume in order to reach the air-cathode surface through the diffusion thickness, L . Current is limited by the transport of oxygen through the gas diffusion layer and reaction on the catalyst surface to use four electrons:



For given boundary conditions with all oxygen reacting on the catalyst surface ($C_o=0$), the limiting current takes the following form in flat configuration:

$$I_{lim} = n \times F \times D_{eO_2} \frac{C_b}{L} \quad (3)$$

and in cylindrical configuration

$$I_{lim} = n \times F \times D_{eO_2} \frac{C_b}{r_1 \ln(r_2/r_1)} \quad (4)$$

The solution for flat geometry is plotted in Fig. 5 for two different diffusion coefficients as a function of diffusion media thickness with the assumption of no limitation from the structure (no porosity and tortuosity effect). An order of change in diffusion coefficient caused the same magnitude of change on the limiting current.

Variation of limiting current density with MTL thickness as a function of porosity is plotted in Fig. 6 with the assumption of a 0.01 $\text{cm}^2 \text{s}^{-1}$ diffusion coefficient for oxygen. There was about a 75% current reduction when porosity was changed from 0.8 to 0.2. A similar reduction was calculated as the diffusion

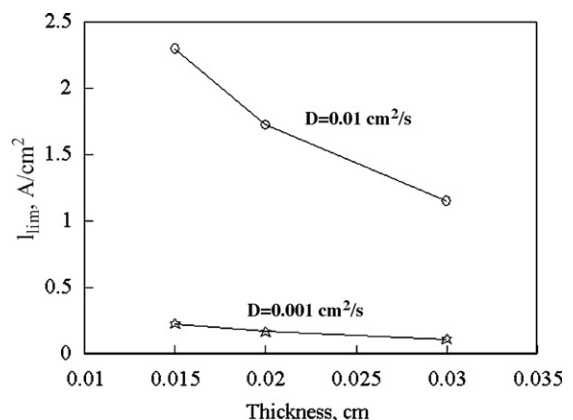


Fig. 5. Calculated limiting current density for passive air diffusion with varying diffusion coefficient and cathode mass transfer layer thickness (porosity (Θ) = 1).

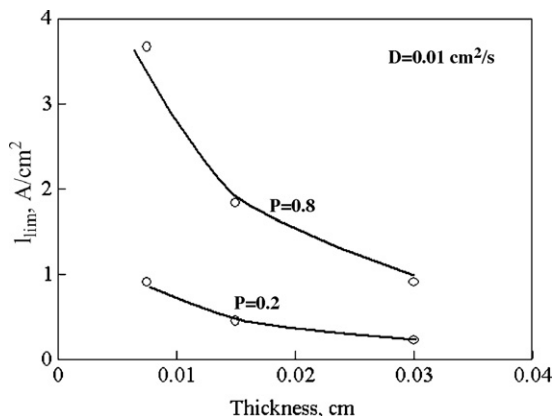


Fig. 6. Calculated limiting current density for passive air diffusion with varying cathode mass transfer layer thickness and porosity (θ^τ form where tortuosity (τ) = 1) at $D = 0.01 \text{ cm}^2 \text{ s}^{-1}$.

media got thicker. In these calculations, tortuosity was assumed to be 1.

Fig. 7 compares the tortuosity effect on limiting current for two different porosities. When tortuosity was increased for a given porosity, limiting current was reduced due to the extended path for oxygen diffusion. That impact became less significant for thicker samples. Therefore, thinner samples with a less tortuous path and lower porosity can approach the performance of higher porosity material with high tortuosity.

When the volume and weight efficiency of flat and cylindrical configurations are compared, elimination of the cathode plate and a larger cathode area provide advantages for cylindrical design. In the conventional design of a cylindrical fuel cell, the air cathode is located on the outer surface of the structure. The surface area of the MTL and the cathode may exceed the anode surface area in the cylindrical configuration. This provides some advantages, which compensates for polarization losses from the cathode. Fig. 8 shows effect of cathode mass transfer layer thickness on limiting current density as a function of cell radius. When limiting current for flat design (with 150 μm MTL) and cylindrical design were compared, for a radius of 0.2 cm, the cylindrical design had about an 8 mA cm^{-2} higher current density than the

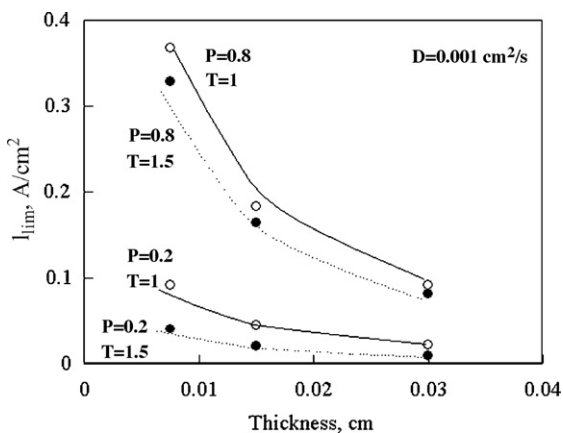


Fig. 7. Calculated limiting current density for passive air diffusion as a function of cathode mass transfer layer thickness with varying porosity and tortuosity at $D = 0.001 \text{ cm}^2 \text{ s}^{-1}$.

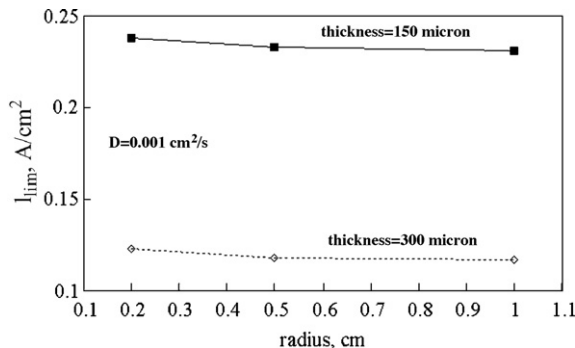


Fig. 8. Calculated limiting current density as a function of cell radius showing effect of cathode MTL thickness.

flat design for a given diffusion coefficient. Higher diffusion coefficients made the limiting current difference between flat and cylindrical configurations larger. Similarly, advantages of cylindrical design for volume efficiency can be demonstrated by the following example. The lowest limit for the diameter of the cell that can be constructed is the curvature diameter of expanded graphite without breaking. Four-millimeter diameter cylindrical cells have been constructed. This corresponds to 10 cm^2 active area and 1 cm^3 volume with 8 cm length. In order to have a similar surface area with the same thickness (4 mm) and length (8 cm), the width of the flat cell must be 1.2 cm. These dimensions correspond to a 4 cm^3 volume with flat design. In fact, due to having nuts and bolts to hold everything together, the overall thickness of the flat cells will be larger. This means that if a cylindrical cell achieves similar current densities as the flat system, the volumetric density will be four times higher with cylindrical design.

3.3. Testing results

After assembly mentioned in Section 3.1 was constructed, the cylindrical fuel cell was initially run at open circuit potential (OCP) with hydrogen flowing. Fig. 9 shows the stability of the open circuit potential for about an hour. Considering no gasket was used in the assembly, it was a very stable and high open circuit potential response.

Fig. 10 shows total fuel cell impedance in a 5 cm^2 cell taken following OCP measurements and after testing is completed. Ini-

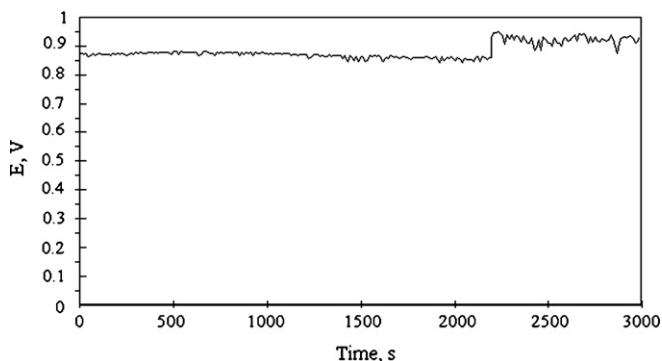


Fig. 9. Stability of open circuit potential for air breathing passive cylindrical fuel cell at room temperature for 3000 s.

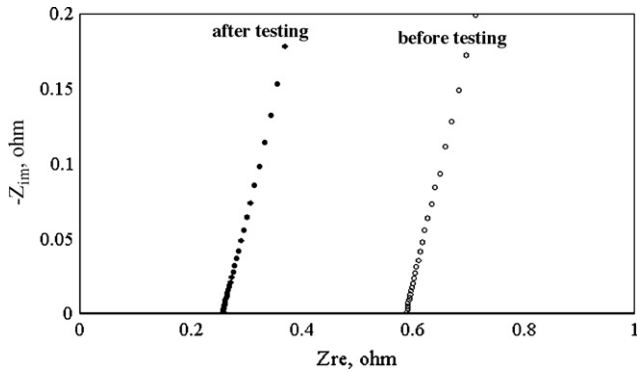


Fig. 10. Cylindrical cell impedance before and after testing under passive air conditions at room temperature.

tial OCP impedance was reduced to about 0.25 ohm after testing due to better humidification and conditioning under polarization. This response was also reflected in the performance for a day-to-day increase in power density.

Fig. 11 shows the polarization response for the cell with 6 ml min^{-1} hydrogen flowing through a small electrolyzer. The objective of the testing was to investigate if self-sealing of the assembly was possible and how it was related to performance. It was shown that the system self seals without any need for a gasket through non-perforated edge of the GRAFCELL[®] mass transfer layer. In order to get better polarization response, there is a need for individual cell component optimization, which includes size of the perforations and micro porous layer optimization. Fig. 12 is obtained under 400 mA total current. Day to day change in response after 11 h of operation was in positive direction for cell performance improvements. It is commonly observed that cell performance gets better and better after several days of testing. Sharp voltage drops were due to interruptions to the hydrogen supply. Fig. 13 is obtained during constant current polarization of the fuel cell. One temperature probe was placed on the surface of the air breathing side and the other thermocouple on the fuel outlet. There was a temperature difference of about 5°C or less between the fuel outlet and the surface of the cell. This difference was mainly due to formation of water on the cathode side. Evaporating water quickly cooled off the cell on the cathode side. Thermal advantages of expanded graphite (approximately $200 \text{ W m}^{-1}\text{K}^{-1}$ surface thermal con-

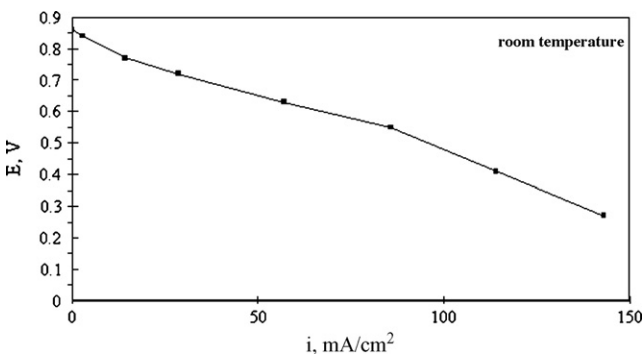


Fig. 11. Performance of cylindrical cell at room temperature using hydrogen and passive air as fuel and oxidant.

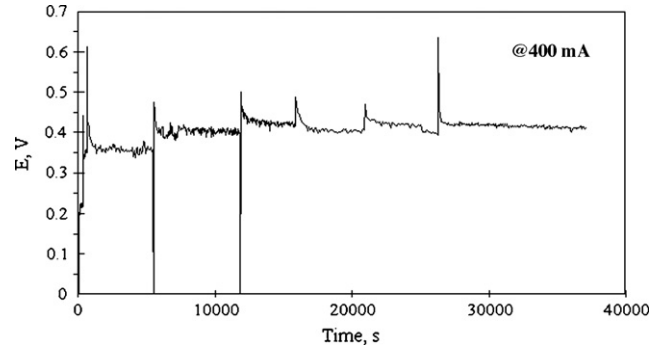


Fig. 12. Voltage response of cylindrical passive cell at 400 mA constant current tested with hydrogen fuel at room temperature without humidification.

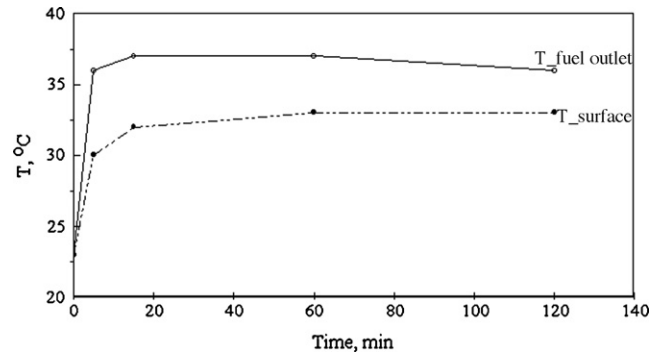


Fig. 13. Passive cylindrical fuel cell temperature profile on the airside surface (T_s) and fuel outlet (T_o) at 400 mA total current.

ductivity) minimized this temperature difference throughout the cell.

4. Conclusions

A mathematical analysis describing diffusion of oxygen to the air cathode in two different geometries was performed and analyzed, indicating higher efficiencies with cylindrical design. A refillable and replaceable fuel cell concept was proposed for the first time around that design. GRAFCELL[®] mass transfer layer technology allowed diameters smaller than 2 mm to be formed to construct cylindrical fuel cells with no additional gasket material. Proposed technology can be quickly applicable to liquid fuel cell platform for portable power sources. A manifold system with electronic circuit management may allow users to refill or replace individual cells when necessary instead of replacing the whole power source.

Further performance optimization of a passive fuel cell system could be done through modification to the mass transfer layer. Perforated MTL with open areas ranging from 1 to 30% were made under consideration for passive operation. On the cathode side, balance between air diffusion (large open area) and water removal (small open area) with reduced diffusion path length needs to be established with optimum micro porous layer thickness. On the anode side with liquid fuel, smaller open area is needed for optimum liquid fuel release without causing crossover.

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