

Design, fabrication, and initial testing of a miniature PEM fuel cell with micro-scale pyrolyzed carbon fluidic plates

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Abstract

Carbonization of machined polymers is a method of creating carbon structures with small feature sizes without having to directly machine carbon (a difficult and expensive process). Pyrolyzed carbon fluidic plates with feature sizes less than 1 mm are used to create a miniature fuel cell. Epoxy is used to seal the fuel cell and water is directly applied to exposed Nafion[®] to hydrate the membrane. The use of miniature carbon fluidic plates will allow for fabrication of 3D (non-planar) proton exchange membrane fuel cells utilizing carbon bipolar plates. Initial test results of the fuel cell are given.

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1. Introduction

The explosion of power-hungry mobile electronics has created a so-called “power gap.” Current mobile power solutions including Li-ion technology are not able to meet the increasing power demands of portable devices. This is exacerbated in future devices due to increasing integration of functionality and because transferring of large amounts of data increases power demands. One reason that battery technology cannot keep up with the tremendous rate of development of integrated circuit (IC) technology (Moore’s law) is because to increase battery capacity, methods of cramming more energy into a limited volume must be devised. In the case of IC technology, more and more functionality has been crammed onto limited areal real estate by patterning smaller/finer features onto a silicon substrate.

One technology that has the promise of replacing batteries in mobile applications is the fuel cell [1–4]. Fuel cells offer the following advantages over other mobile power sources:

- (1) Fuels used in fuel cells typically have much higher (approximately 10× according to reference [5]) energy densities than their battery counterparts [4,5].
- (2) Instant replenishment of energy [6] (instead of charging a battery for an extended amount of time, a fuel cell cartridge could be replaced).
- (3) Fuel cells are clean and efficient [6,7].
- (4) To increase the power density of a fuel cell, one only needs to increase the surface-to-volume ratio within a fuel cell. This is a much simpler task than engineering new material chemistries.

Moreover, a microfabricated fuel cell design offers the following benefits [8]:

- (1) The electrochemical reaction, heat transfer as well as mass transfer are all surface phenomena. As a device is miniaturized, the surface-to-volume ratio of the entire device increases because, typically, area scales with l^2 while volume scales with l^3 . Thus, the surface-to-volume ratio, in general, scales with proportion to $l^2/l^3 = 1/l$. This is directly applicable in the case of heat dissipation. In the case of electrochemistry, the scaling laws may be slightly more complex. The layered architecture of a typical PEMFC (proton exchange membrane fuel cell)/DMFC (direct methanol

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fuel cell) will lend itself to scale similar to a planar device. For an idealized entirely 2D layered device, the surface-to-volume ratio is independent of scaling. Since fuel cell layers are not ideal planar structures, it is expected that miniaturizing a fuel cell will still increase the surface-to-volume ratio in terms of the effective electrochemical surface area. Whether scaling down or scaling up, it is advantageous for the electrochemical device to have a large surface area relative to the volume.

- (2) Increased power density (due to the high surface-to-volume ratio).
- (3) Low cost (due to less material cost per unit).
- (4) High efficiency (due to the high surface-to-volume ratio and the corresponding increase in triple phase boundaries).
- (5) Increased catalyst utilization (because microfabrication techniques allow more control over catalyst deposition).
- (6) Reduced system complexity.
- (7) Novel fuel cell applications.
- (8) It is easier to maintain a homogeneous environment within a small area.
- (9) Lower internal resistance (due to shorter conductive paths).
- (10) The balance of plant can be reduced, further reducing total weight and volume.
- (11) Smaller fluidic channel sizes allow efficient mass transport (for serpentine flow patterns, the flow velocity is inversely proportional to the square of the length scale [9]).

1.1. Miniature fuel cells

Even though efficient large-scale fuel cells (approximately 1–200 kW [6]) have been developed and commercialized, it has proved much more challenging to create efficient miniature fuel cells. It is difficult to miniaturize traditional fuel cell designs (such as fuel cell stacks) to build portable fuel cells because the materials and manufacturing methods are just not available for microfabrication. One reason for this is because cost and time effective miniaturization processes have not been developed for many of the materials such as graphite, which is used in large fuel cell designs. There have been attempts at replacing the high purity graphite bipolar separators that are used in conventional PEM fuel cells with other materials such as stainless steel, aluminum, titanium, and conductive plastics, but none of these materials have replaced carbon as the material of choice due to life-time (caused by corrosion) and contact resistance issues [8]. Material issues are even more paramount in microelectromechanical system (MEMS)-based fuel cell designs because MEMS fabrication technology has traditionally been limited to a small palette of materials (silicon, metals, glass, some ceramics, etc.). Furthermore, since the miniaturization processes used in MEMS-based devices are mostly derived from IC technology, most processes are surface machining techniques [10]. There has thus been a push towards planar monolithic MEMS fuel cell designs [6,11,12]. Other non-planar fuel cell designs involve complicated fabrication schemes that are not manufacturing amenable [6,13]. In this contribution, a method of fabricating miniature carbon fuel cell components through carbonization of polymers will be introduced.

Several fuel cell types have been proposed for miniature fuel cell systems including borohydride fuel cells, reformed methanol to hydrogen fuel cells, formic acid fuel cells [14], bio-fuel cells (BFCs), and direct methanol fuel cells (DMFCs) [1,6,7,15]. Currently, the direct methanol fuel cell (DMFC) [15], which uses methanol directly as a fuel without the need for a reformer is regarded as the most promising technology in the near term for miniature fuel cells for portable applications [16]. Unfortunately, the direct methanol fuel cell also is considered as one of the most difficult fuel cell technologies due to problems such as methanol crossover and catalytic inefficiency [15,17]. Most of the research done in miniature fuel cells has been focused on the DMFC architecture, which is based on a proton exchange membrane (PEM) design. The PEMFC will be the emphasis of this paper.

There have been past efforts in miniaturizing fuel cell systems [18,19]. Fabrication methods have included printed-circuit technology [18], silicon and MEMS technology [5,8,11,13,18–21], and aluminum-covered SU-8 negative photoresist [22–24]. MEMS-based microreactor systems [25], porous silicon processing-based bilayer fuel cells [5,13,19], and other MEMS-based fuel cell systems have been proposed in previous literature [5,8,11,20,21]. The fabrication of fuel cells using conventional MEMS technology is time-consuming and entails many steps.

There are two different approaches for fabricating fuel cells using MEMS technology [5]. One approach that leverages the fact that most MEMS technology is based on surface micro-machining is the monolithic MEMS fuel cell design. In this approach, the bipolar approach of larger fuel cells explained in the previous sections is not used. Instead, multiple cells are fabricated on the same plane. Approaches such as the “flip-flop” interconnect method [11,18] are used instead of stacking to connect the cells in series. The other approach is to follow the design principles of larger fuel cells and stack several cells on top of each other. The current trend is toward monopolar planar designs [12].

Reference [5] compares bipolar and monolithic MEMS fuel cell designs. Bipolar designs had higher current densities when measured relative to both cathode and substrate areas. Bipolar designs had higher volumetric current densities, higher power densities, and less complicated electrical contacts. Even though the authors only compare designs based on silicon technology, bipolar designs showed an overall advantage over monolithic designs. Directly miniaturizing current graphite fluidic plate designs has proven difficult due to the brittleness of the material [11,26]. The carbon microforming technique introduced in Section 2 may provide the tools necessary for creating miniature carbon fuel cell components. The authors believe that with the use of carbon as the bipolar plate material, the bipolar design will prove to be even more attractive.

1.2. PEMFC/DMFC fuel cell constraints

Each component within a fuel cell needs to adhere to physical, chemical, and material constraints that are sometime conflicting. For example, the membrane (electrolyte) must have high ionic

conductivity (for Li ions) but must not provide a direct path for electron flow. It also must act as a mechanical structural member and have excellent sealing capabilities [7,8]. Currently, the most popular material for PEMFCs and DMFCs is sulfonated PTFE (polytetrafluoroethylene), sold under the name, Nafion[®] by Dupont. The gas diffusion electrode must provide high electrical conductivity, high gas diffusion, electrochemical stability, low contact resistance, and must provide a path for water evacuation to prevent flooding [7,8]. PTFE-coated carbon paper is currently used for gas diffusion electrodes in most conventional PEM and DMFCs. The main hydrogen or methanol oxidation reaction occurs at catalyst sites where gas (for the fuel or oxidant), electrolyte (for the ion transport), and conductor (for electron transport) must meet. These sites are called triple phase boundaries or triple points. The number or area of these triple phase boundaries must be maximized for high efficiency with low catalyst loadings. The catalyst layer must provide such an environment. The optimal catalyst size for a platinum catalyst was found to be $\sim 30 \text{ \AA}$ [15]. For the catalyst support carbon, it was observed that using low surface area carbons such as Acetylene Black with a BET (Brunauer, Emmett and Teller) surface area of $50 \text{ m}^2 \text{ g}^{-1}$ did not allow a high dispersion of the catalyst particles, but resulted in poor mass transport because of the lack of microporosity [15]. Carbon blacks with high surface area such as KETJEN black which has a BET surface area of $1000 \text{ m}^2 \text{ g}^{-1}$ have high mass transport through micropores and allow a high dispersion of catalyst, but the same micropores hamper homogeneous distribution of catalyst particles [15]. Vulcan XC seems to be the best compromise [15] using widely available carbon blacks. It is difficult, if not impossible, to determine the exact amount of triple phase boundaries in a PEMFC because of the complexity of the catalyst support structure [27]. It has already been observed that mechanical roughening of surfaces increases performance in MEMS fuel cells [28]. The same researchers state that more dramatic increases in surface-to-volume ratio can be achieved through photolithography and micromachining. The authors believe that this dramatic increase in surface-to-volume ratio (along with an increase in triple phase boundaries) can be achieved by converting photolithographically defined or micromachined polymer structures into carbon (a process coined as carbon microelectromechanical systems, or C-MEMS [29–37]).

1.3. C-MEMS fuel cell components

Machined graphite is used in large-scale fuel cells as the bipolar plate material. In a fuel cell, the voltage from each cell is typically more or less 1 V depending on the losses occurring. Several cells need to be stacked in series to create a “useful” voltage. Bipolar plates are an optimal method of stacking cells. They act as a conductive separator between cells, separating the fuel from the oxygen. The fluidic channels of a bipolar plate serve to spread the gas across the entire cell. A bipolar plate must exhibit the following properties [26]:

- (1) High electrical conductivity.
- (2) Resistance to corrosion.
- (3) Chemical compatibility.

- (4) High thermal conductivity.
- (5) Low leakage of gasses.
- (6) High mechanical robustness.
- (7) Low weight.
- (8) Manufacturability.
- (9) Low cost.

Graphite is the material of choice for current PEMFCs and DMFCs because it satisfies all of the criteria listed above with the exception of manufacturability, low cost, and mechanical robustness [26]. Graphite bipolar plates are relatively difficult to manufacture, expensive, and are not mechanically robust due to costly machining requirements and the intrinsic brittleness of the material [26]. Surprisingly, the machining of graphite bipolar plates is so expensive that the cost of the plates can add up to half the cost of the entire fuel cell [26]. In the case of miniature fuel cells, graphite has not been the material of choice because of difficulties in machining [11,26] and because it has traditionally been easiest to utilize integrated circuit (IC) and microelectromechanical systems (MEMS) techniques to create small structures.

The specific requirements for bipolar plates differ for each application/device and will be size-dependent. As an example, the Department of Energy FreedomCAR project performance targets for bipolar plates used in automotive fuel cells to be met by the year 2010 are given below [38]:

- Cost: $\$ 6 \text{ kW}^{-1}$.
- Weight: $< 1 \text{ kg kW}^{-1}$.
- H₂ permeation flux: $2 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2}$ at 80°C , 3 atm.
- Corrosion: $< 1 \mu\text{A cm}^{-2}$.
- Electrical conductivity: $> 100 \text{ S cm}^{-1}$.
- Area specific resistance: $0.01 \Omega \text{ cm}^2$.
- Flexural strength: $> 4 \text{ MPa}$ (crush).
- Flexibility: 3–5% deflection at mid-span.

Most IC and MEMS techniques are planar surface micromachining techniques. Bulk micromachining techniques such as KOH etching of silicon can be used to create 3D bipolar plate designs, but these techniques are typically slow and uneconomical. Because of these reasons many in the field of miniature fuel cells support planar designs (many utilizing “flip-flop” connections, see previous section). The planar designs have advantages in applications where the device that is to be powered is flat and has a large area (displays, etc.), but the fuel cells cannot be used in applications where no large area is provided. The disadvantage of these designs is that a fuel cell must be spread over a large area. In order to create a compact volumetric package, an architecture using bipolar plates must be used. Carbon has an advantage that it is the material used in larger fuel cells, thus much about its use in the fuel cell environment has been clarified. It is also inert in the fuel cell environment unlike metals, most of which corrode when used in a fuel cell. The noble metals that are inert within a fuel cell environment are expensive.

The authors believe that C-MEMS [29–37] technology will allow relatively simple fabrication of miniature stacked bipolar PEM fuel cells. C-MEMS is a fabrication technique in which car-

bon devices are made by treating a pre-structured organic material to high temperatures (typically 900 °C and higher) in an inert or reducing environment. Although some shrinkage occurs, the geometry is largely preserved during the carbonization process because the shrinkage is isometric. The details of the fabrication process using SU-8 photoresist are detailed in a separate paper [30]. Using the C-MEMS process, complex micro-scale 3D electrodes with high aspect-ratios can easily be shaped and patterned using conventional lithography. The electrical properties of the C-MEMS carbon derived from SU-8 and AZ4620 photoresists has been quantified [31], and has been found to be similar to glassy carbon. The capability of creating micro- and nano-scale 3D carbon structures has opened up a wide range of new applications for pyrolytic carbon including micro batteries [37], glucose sensors, super capacitors, bio fuel cells, dielectrophoretic electrode arrays for micromanipulation of micro- and nano-particles [39], electrodes for bio-recording/stimulation, and electrode arrays for DNA hybridization and detection.

The results from the electrical characterization for C-MEMS carbon [31] show that photoresist that has been treated to high temperatures (~ 1000 °C) has a resistivity close to commercially available glassy carbon. For a thin bipolar plate, these resistivities should be more than sufficient for a working fuel cell platform.

C-MEMS technology [29–37] allows fabrication of miniature fuel cell components using a material (carbon) already used in large-scale fuel cells. When applied to miniature fuel cells, C-MEMS technology can offer the following benefits:

- (1) Novel bipolar (instead of planar/monolithic [11]) design with carbon bipolar plates. Planar/monolithic designs are pertinent for applications where large areas are available. On the other hand, in cases where a small three-dimensional package is preferred, bipolar designs are much better suited. A bipolar (instead of planar/monolithic) design with carbon bipolar plates will allow small-sized volumetric packaging of miniature fuel cells.
- (2) Because the bipolar plate fluidics, gas diffusion layer, and catalyst support layer are all made of carbon, they can be integrated and fabricated into a single homogeneous structure. This reduces complexity and internal resistance while increasing mechanical robustness.
- (3) Increased surface area using nanomaterials and controlled microtexture (using a polymer binding agent). Techniques of increasing the surface area of C-MEMS have been developed (unpublished work). These techniques can be used to further increase surface area for fuel cell applications of C-MEMS structures.
- (4) Binding using C-MEMS materials for enhanced electrical contact (in C-MEMS technology, physical binding agents can also act as electrical binding agents because they are converted into carbon during the pyrolysis process).
- (5) Control over the carbon precursor allows materials engineering of the carbon itself.
- (6) Natural materials can be carbonized to create porous membranes with large surface/volume ratios and can be enhanced further with nanomaterials.

1.4. Preliminary experiments: physical/electrical binding, substrate-less C-MEMS, and metal/carbon structures

Before beginning development of a C-MEMS-based miniature fuel cell, several experiments were performed to gauge the feasibility of (1) using a polymer binder to bind two different materials together having the polymer binder act as both a physical and electrical binding material and (2) creating carbon structures free of a substrate (substrate-less C-MEMS).

Initial tests using AZ P4620 photoresist (Clariant) have been performed. The photoresist was used to bind polyimide (Kapton[®]) sheets as well as wood pulp paper. After pyrolysis, the AZ P4620 proved to be a satisfactory physical and electrical binding agent.

Primary efforts in creating substrate-less carbon structures were concentrated on the material of choice at that time, SU-8 negative photoresist (Microchem—Newton, MA). Layers of SU-8 were spun on, soft-baked, exposed, hard-baked, then removed from a flexible substrate (Kapton[®] films obtained from Fralock—Canoga Park, CA). These SU-8 films were converted into carbon, but the SU-8 and carbon films were both too brittle to be handled efficiently. It was concluded that thicker carbon films made from a different polymer or a thin substrate of another material is needed to provide structural integrity to the C-MEMS structure.

Efforts have been made to coat metals (gold, steel, cast iron, stainless steel, copper, nickel) with polymers (various oils, photoresists, epoxies, polyurethanes, lacquers, polyimides, etc.) and then to pyrolyze the carbon to create an inert carbon structure, but either (1) the surface energy of the metal cause the metal to change shape (gold), (2) the polymer evaporated instead of carbonizing (oils, polyurethanes, lacquers, etc.), or (3) the thermal coefficient of expansion difference between the two materials lead to cracking of the carbon layer.

C-MEMS posts have been fabricated on thin metal films (Fig. 1). Initial attempts on thin gold films had failed due to balling up of the gold films at the high pyrolysis temperatures. Other metals have shown promise as suitable substrates for C-MEMS devices. Smaller structures seem to survive the pyrolysis

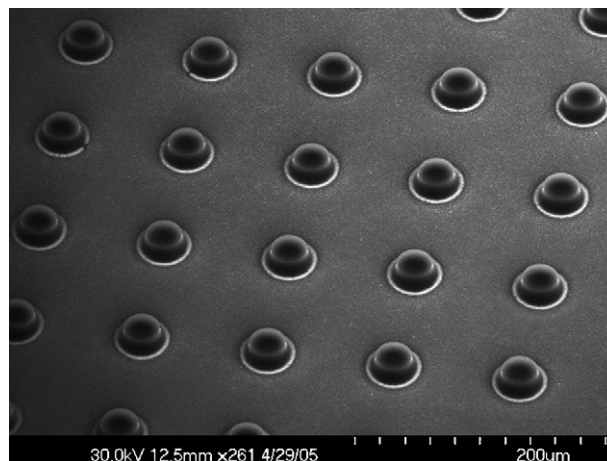


Fig. 1. C-MEMS posts fabricated on a thin metal film.

process when patterned on metal substrates due to less internal stress within the structures.

1.5. Charring characteristics of polymers

After experimentation with many different types of polymers and coatings including various oils, photoresists, epoxies, polyurethanes, lacquers, polyimides, etc., it was found that most (oils, polyurethanes, and lacquers) coatings evaporated or gasified during the pyrolysis process. Other polymers changed shape (melted) before being converted into carbon (most of the positive photoresists). Self-charring polymers are polymers that create a layer of char (carbon) instead of melting or directly releasing large amounts of gas when treated to heat [40]. When creating carbon structures from a polymer precursor, it is advantageous to retain as much carbon as possible from the hydrocarbon. Charring characteristics of a polymer are thus important for materials used for C-MEMS. Charring characteristics can be improved by cross-linking or chain stiffening of thermosetting polymers and, in general, charring polymers tend to have high melting, glass transition (T_g), and operating temperatures. High-temperature polyimides have the highest glass transition temperature (typically $\sim 400^\circ\text{C}$) out of all of the widely available polymers and thus, polyimide was selected as the best candidate material for fabricating the miniature fuel cell. Kapton[®] is a commonly used Dupont polyimide film that has no measurable melting temperature and has a glass transition temperature between 360 and 410°C [41]. A film of Kapton[®] was pyrolyzed at 1000°C . Unlike the films of SU-8 negative photoresist, the pyrolyzed Kapton[®] film was not brittle and did not break into pieces when handled. The film exhibited excellent electrical conductivity after pyrolysis. PI-5878G is a wet-etchable high- T_g standard spin-on polyimide available as part of the SP series from HD Microsystems. The T_g of an applied film is 400°C . Initial experiments were performed with PI-5878G to test whether the material could be used to physically and electrically bind materials to create a homogeneous carbon structure. Initial tests using sheets of Kapton[®] and paper demonstrated that, after pyrolysis, the PI-5878G provided an excellent physical and electrical bond. The use of polyimide solids and PI-5878G is an attractive method for creating homogeneous carbon structures because, even before pyrolysis, the structure is a homogeneous polyimide structure.

Kapton[®] is not available in thick (>5 mil) films. For applications such as the miniature fuel cell described in the following

text, thicker polyimide films must be used. Cirlex[®] is a Dupont material consisting of 100% Kapton[®]. Sheets of Cirlex[®] consist of Kapton[®] sheets bonded using adhesive-less bonding technology [41,42].

2. Experimental/materials and methods

2.1. Design and materials

Based on the preliminary studies performed (presented in the previous section), polyimide (20 mil Cirlex[®] sheet and PI-5878G) was selected to be used as the material for use in creating a microfluidic carbon plate. Although future attempts will be made in creating a full fuel cell stack using microfluidic bipolar plates, two monopolar plates were fabricated for the initial prototype to demonstrate proof-of-concept. Additionally, in future designs, the entire flow channel/electrode (catalyst support layer gas diffusion layer) assembly may be fabricated as a homogenous single structure for improved mechanical (increased robustness, less sealing needed) and electrical (reduced internal resistance) characteristics. In the initial prototype, commercial electrodes were used.

The design of the C-MEMS fuel cell prototype is shown in Fig. 2.

In past studies, SU-8 microfluidic channels covered with aluminum were used to determine optimum flow channel dimensions for fuel cells [23]. It was argued that small channels offered the following advantages over designs with large channel dimensions [23]:

- (1) Mass transport due to a higher flow velocity can be maximized while maintaining gas stoichiometry.
- (2) “Dead zones” underneath structures can be minimized.

Moreover, smaller channel diameters allow for thinner fluidic plates that could allow for lower resistances. However, it was found that there was an optimal size that provided the best performance for fuel cells because, once the fluidic channels became too small, flooding occurred [9,23]. One other important design consideration to take into account when designing a fuel cell with small channel dimensions is that smaller channel sizes will increase the pressure drop within the channels. The total length of the channel must be short to insure that the pressure drop needed to drive the gas through the fluidics is not

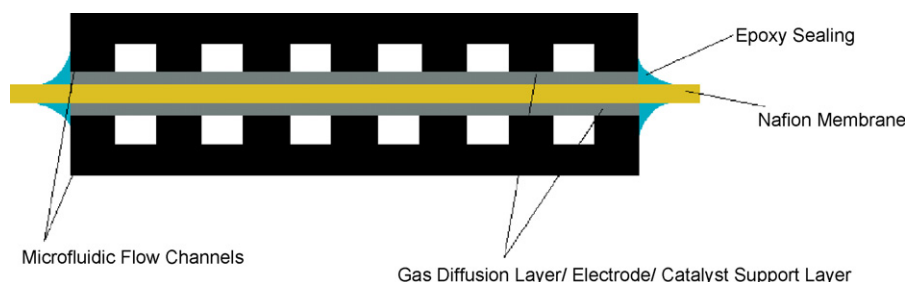


Fig. 2. Design for the C-MEMS fuel cell. In future designs, the carbon microfluidic channel walls will be physically and electrically bonded with the gas diffusion layer, electrode, and catalyst support layer during fabrication. This will result in all of the carbon within the fuel cell forming a single integral structure.

too great. The optimal channel size was found to be approx. 100 μm in one study [23] and approximately 500 μm in another [9]. Because flow channels with features sizes of 500 μm can be easily machined instead of having to use photolithography, a channel size of 500 μm was used for the miniature fuel cell prototype.

In addition to proving feasibility of miniature carbon fluidic plates for use in miniature fuel cell stacks, the initial prototype utilized a novel sealing method for micro fuel cells and may provide a method for simple water management within micro fuel cells.

In many stacked fuel cell architectures, pressure is applied to the top and bottom of the fuel cell to ensure adequate electrical connection between the layers and gaskets are used for sealing the outer edges of the fuel cell. Leakage is a problem in these designs. Epoxy is proposed as a permanent sealant for miniature fuel cells. Epoxy is used as a permanent sealant because of its resistance to acidic environments and its mechanical stability. To the best of our knowledge, epoxy did not poison the fuel cell catalysts or significantly affect the Nafion[®] membrane within the fuel cell.

Finally, water management is a critical issue in miniature fuel cell designs. The method described in this paper may be used to prevent drying of the membrane without the need of humidifying the dry hydrogen. Further research is being performed to determine the extent of this hydration. The Nafion[®] membrane is larger than the other components so that a portion of the membrane is exposed. Nafion[®] is left exposed to the outside environment and water can be supplied to the inner membrane by hydrating the exposed portion. The hygroscopic property of Nafion[®] is utilized to hydrate the inner Nafion[®] membrane by supplying moisture to an external portion.

2.2. Fabrication

A simple summary of the fabrication process is given as follows:

- (1) Fluidic channel walls and separators are machined from high-temperature polymer sheets and bonded together to create fluidic plates.
- (2) The structures are converted into carbon. A physical binder acts also as an electrical binder.
- (3) Commercial fuel cell electrodes are combined with an activated Nafion[®] membrane to create a membrane electrode assembly (MEA).
- (4) The MEA, fluidic plates, and gas inlet/outlets are brought together and epoxy is used to seal the entire fuel cell structure.

The detailed fabrication steps are listed below.

2.2.1. Fluidic plate construction

- (1) Cirlex[®] (Fralock—Canoga Park, CA) sheets were finely machined using a circuit board milling tool (T-Tech—Norcross, GA). Cirlex[®] is a Dupont polymer sheet made by bonding several Kapton[®] sheets to create a thicker



Fig. 3. Machined Cirlex[®] fluidic walls. Each design is 1 cm \times 1 cm in dimension.

sheet. Cirlex[®] is relatively straightforward to machine because it does not melt and adhere to the end mill bit. The Cirlex[®] sheet was placed on an adhesive to hold the machined pieces in place after and while machining. Twenty mil (\sim 500 μm) thick Cirlex[®] sheets were machined with 500 μm diameter end mills in a T-Tech circuit board milling tool to create the fluidics (Fig. 3) (past literature has suggested that fluidic channel sizes between 100 μm [23] and \sim 500 μm [9] are optimal. Fabrication using 100 μm polymer sheets (SU-8 and Kapton[®]) has been attempted, but the carbon films cracked too easily when handled manually. Although 500 μm sheets were used for the initial prototype because of ease of handling, thinner sheets can provide lower internal resistance as well as possibly maximizing mass transport). A serpentine flow pattern was used, but other flow patterns such as interdigitated or spiral interdigitated patterns may be used. Fluidic pieces as well as blank/bare 1 cm \times 1 cm squares (Fig. 4) were cut out of the Cirlex[®] sheet.

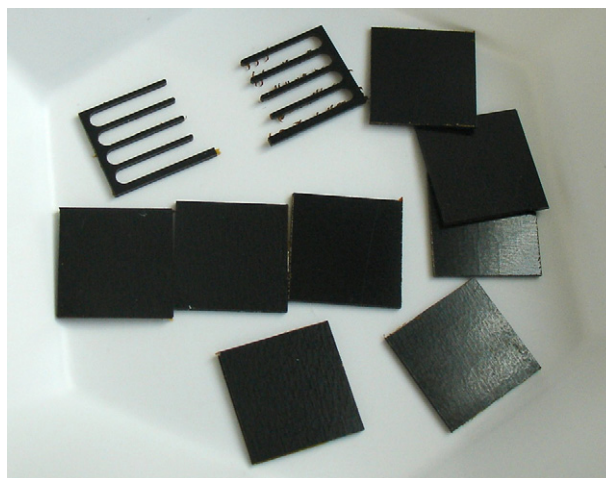


Fig. 4. Bare 1 cm \times 1 cm squares.

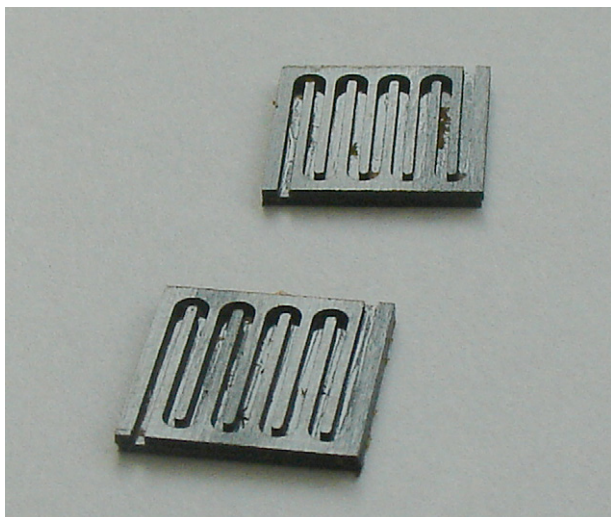


Fig. 5. Fluidic plate structures before carbonization.

(2) The machined pieces are bonded together with PI-5878G (HD Microsystems) polyimide. The fluidic pieces are kept aligned with each other by keeping them adhered to an adhesive material. After machining, the fluidic pieces were first carefully transferred to polyimide tape. This was done to prevent the original adhesive material from melting while the PI-5878G was cured. The fluidic pieces were adhered to the machined blank squares. Squares of 5 mil thick Kapton® has also been used as separators, but thicker Cirlex® is preferred due to the mechanical robustness. The machined Cirlex® parts were cleaned with successive washes of isopropanol, acetone, and again, isopropanol. After drying of the parts with dry nitrogen gas, the PI-5878G polyimide was applied with a cotton swab. The PI-5878G was cured by ramping the temperature at a rate slower than $4\text{ }^{\circ}\text{C min}^{-1}$ to $200\text{ }^{\circ}\text{C}$ on a hot plate. The temperature was held at $200\text{ }^{\circ}\text{C}$ for 1 h. The hot plate was then turned off and the polyimide was left on the hot plate to cool slowly. The polyimide tape was then removed because the pieces were now bonded in place. Fig. 5 shows the fluidic plate before carbonization. Although the fluidic pieces were bonded to one side of the blank squares in the proof-of-concept prototype, the pieces could have been bonded to the top and bottom of these blank squares to create the fluidics for the fuel (hydrogen, methanol, etc.) and the oxidant (air, oxygen, etc.). Such three-layer bipolar plates have been created (see Fig. 6).

(3) The bonded structure is treated to high temperatures in an inert environment to convert the entire structure into carbon. A 1 in. long portion of a steel bar was placed on top of the structure to prevent warping of the fluidic plate during pyrolysis. The entire structure was pyrolyzed in a two-step process in a forming gas (5% hydrogen, 95% nitrogen) atmosphere. An open-ended quartz furnace was used. The temperature was ramped from room temperature to $300\text{ }^{\circ}\text{C}$ in 12 min. The heating element was turned off and the hot furnace was left for 30 min in order to fully cure and heat treat the polyimide. After 30 min, the furnace temperature was $220\text{ }^{\circ}\text{C}$. The temperature was then ramped to $900\text{ }^{\circ}\text{C}$ in

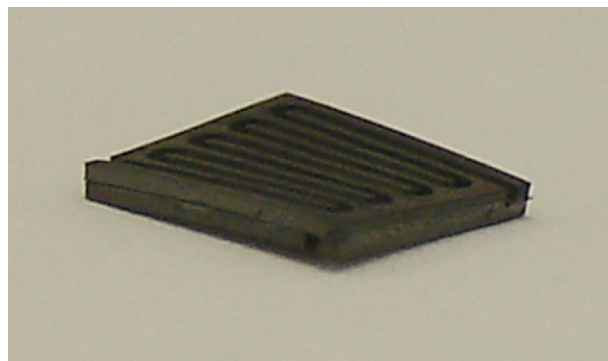


Fig. 6. A three-layer carbon bipolar plate structure made by first bonding Cirlex® fluidic channel walls to a 5 mil Kapton® sheet then converting the entire structure into carbon.

60 min and left at $900\text{ }^{\circ}\text{C}$ for an hour to fully convert the polyimide into carbon. The furnace was turned off and let to slowly cool to room temperature.

(4) It is important to note that there is some shrinkage in the final structure. A 20% shrinkage of length and width was observed. Fig. 7 shows two carbonized fluidic plate structures to the left of a $1\text{ cm} \times 1\text{ cm}$ Cirlex® square. The structures shown in Fig. 5 were carbonized to create the carbon fluidic plates shown in Fig. 7. The shrinkage of approximately 20% can be seen.

2.2.2. Membrane electrode assembly (MEA) construction

- (1) A Nafion® sheet (Nafion® 115 purchased from Electrochem—Woburn, MA was used for the initial prototype. The thickness of Nafion® 115 is 5 mil) is cut to a size that is slightly larger than the fluidic plate size.
- (2) Commercial fuel cell electrodes are cut to the size of the fluidic plate. These commercial fuel cell electrodes are comprised of carbon paper (acting as the gas diffusion layer) with platinum catalyst loaded on one side. The electrodes come pretreated with Teflon® to allow water to pass through easily. The catalyst only needs to be replaced with PtRu on the anode side to create a direct methanol fuel cell. For the initial prototype, an electrode with 1 mg cm^{-2}

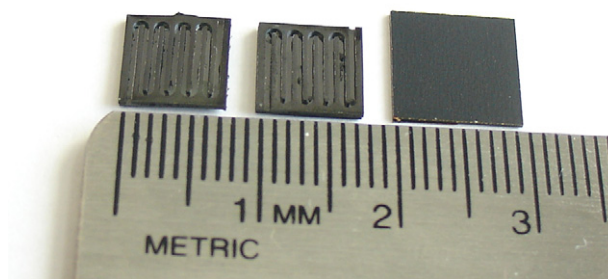


Fig. 7. Two carbon fluidic plate structures are shown to the left of a $1\text{ cm} \times 1\text{ cm}$ Cirlex square. The structures shown in Fig. 5 were carbonized to create the carbon fluidic plates shown in this figure. The shrinkage of approximately 20% can be seen.



Fig. 8. The finished MEA. The liquid shown on the MEA is water.

loading, 20 wt.% Pt/Vulcan XC-72 was used (EC-20-10-7, Electrochem—Woburn, MA).

- (3) Five percent Nafion[®] solution (EC-NS-05-250 ml, Electrochem—Woburn, MA) is brushed on the side of the electrode that has the platinum catalyst. The Nafion[®] solution coated electrodes are placed in a dry and cool environment at room temperature until visibly “dry”.
- (4) The Nafion[®] is activated by a series of heated baths (all at 80 °C): DI water for 1 h, 30% hydrogen peroxide for 1 h, ~10 M sulfuric acid (1:1 dilution of pure H₂SO₄ and DI water) for 1 h, and finally, a short rinse in DI water.
- (5) The Nafion[®] is stored in DI water until fabrication of the MEA.
- (6) To fabricate the MEA, the electrodes are placed on either side of the Nafion[®] sheet and pressed into the Nafion[®] sheet. Although a pressure of ~2 MPa is recommended, a C-clamp was used to press the electrodes into the Nafion[®] sheet. Everything was heated under glassware with a water soaked fabric in order to prevent drying out of the Nafion[®]. The Nafion[®] and the electrodes were ramped to 90 °C for 1 h, to 130 °C for 30 min and the C-clamp was tightened at 130 °C and left at 130 °C for 5 min. The hot plate was shut off and let to cool slowly to room temperature. Fig. 8 shows a photo of the finished MEA.

2.2.3. Integration into a miniature fuel cell

- (1) The carbon structures created in Section 2.2.1 were aligned and placed on the top and bottom of the MEA. The fluidic plate–MEA–fluidic plate assembly was held together with pressure using a C-clamp. Paraffin was used between the C-clamp and the structure to prevent breakage and because paraffin is easily removed.
- (2) Syringe needles (needle size: AWG 26.5) were inserted into the fluidic entrances and exits in order to provide an interface to external gas or fluidic sources. Epoxy was used to seal and hold the needles in place.
- (3) Two-part epoxy was used to seal the fuel cell. It was applied liberally, but the entire Nafion[®] sheet was not covered. The portions of Nafion[®] that are not covered with epoxy will

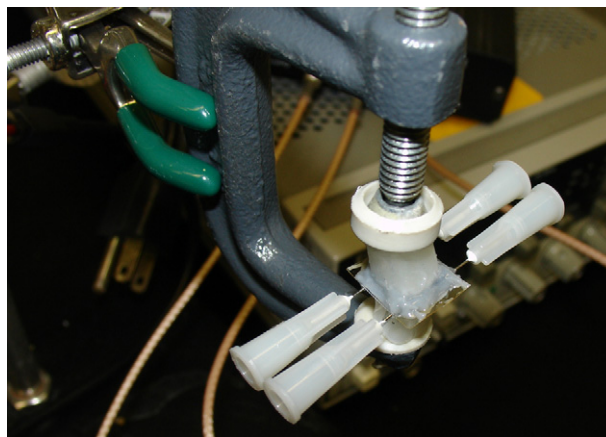


Fig. 9. A photo of the C-clamp assembly and fuel cell with paraffin and epoxy sealing.

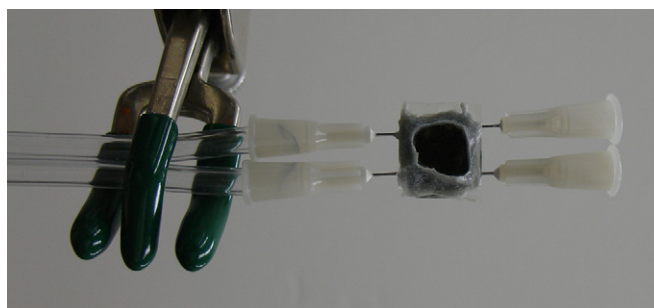


Fig. 10. Photo of the complete fuel cell attached to gas inlets for oxygen and hydrogen shown before wires were added and bonded with silver epoxy. The epoxy sealing, the input and output connections, the carbon electrical contact surface, and the Nafion[®] surface extending beyond the epoxy sealing can be clearly seen in this photo.

be exposed to water/moisture so that the water can diffuse within the fuel cell. This may prove to be a useful water management technique. Fig. 9 is a photo of the C-clamp assembly and fuel cell with paraffin and epoxy sealing.

- (4) After waiting for 48 h for the epoxy to completely cross link, the fuel cell assembly was detached from the C-clamp and the paraffin was removed. The carbon surface that is exposed serves as the electrical contact area (Fig. 10). Wires can be attached to this area using conductive silver epoxy for ease of connection (Fig. 11).

3. Results

An open-circuit voltage of 871 mV was measured when using a crude electrolyzer setup (platinum electrodes in a sodium sulfate solution) at room temperature. The closed-circuit current draw of the fuel cell stabilized at 3.11 mA (with a voltage of 110 mV). The *I*–*V* curve and power of the fuel cell is shown in Fig. 12. The maximum power output was 0.773 mW. Because the fuel cell area is 0.64 cm², the areal power output is 1.21 mW cm⁻². From the *I*–*V* curve, the internal resistance of the fuel cell was calculated to be approximately 210 Ω. Using the same electrode and catalyst loading but at 90 °C and with a pressure of 101 kPa (1 atm) for each gas, a power peak of

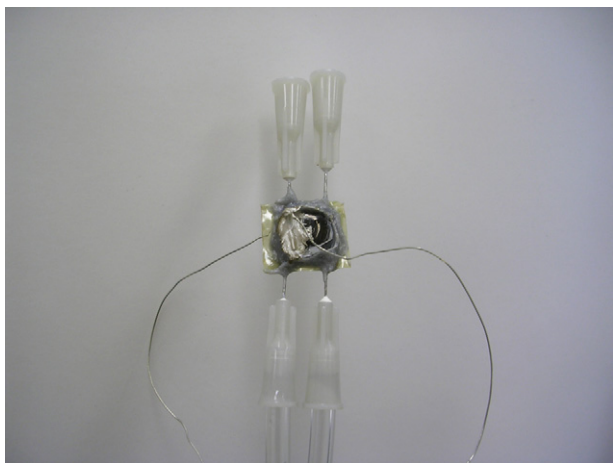


Fig. 11. Photo of the complete fuel cell attached to gas inlets for oxygen and hydrogen after wires were added and bonded with silver epoxy.

6.7 mW cm⁻² was measured [21]. The areal power output for the C-MEMS fuel cell was expected to be lower than 6.7 mW cm⁻² because of the low temperature of operation and the extremely small area of the fuel cell (~500 times smaller than typical portable fuel cells). The small area is also the cause of the large internal resistance. This internal resistance can be minimized by using thinner Nafion® membranes. It was not determined whether the fuel cell was operating at maximum efficiency. It is possible that the open-circuit voltage will increase with a higher pressure fuel/oxygen flow. In future tests, testing with a pressurized hydrogen and oxygen source will be performed at 80 °C. Fig. 13 shows the electrolyzer setup.

Further tests are planned to determine the weight per kW, H₂ permeation flux, electrical conductivity, flexural strength, and flexibility. From past literature, it was found that Kapton® is a material that is easily graphitizable [43–46]. When pyrolysis temperatures less than 1000 °C are used, the Kapton® material remains in an amorphous state, but at pyrolysis tempera-

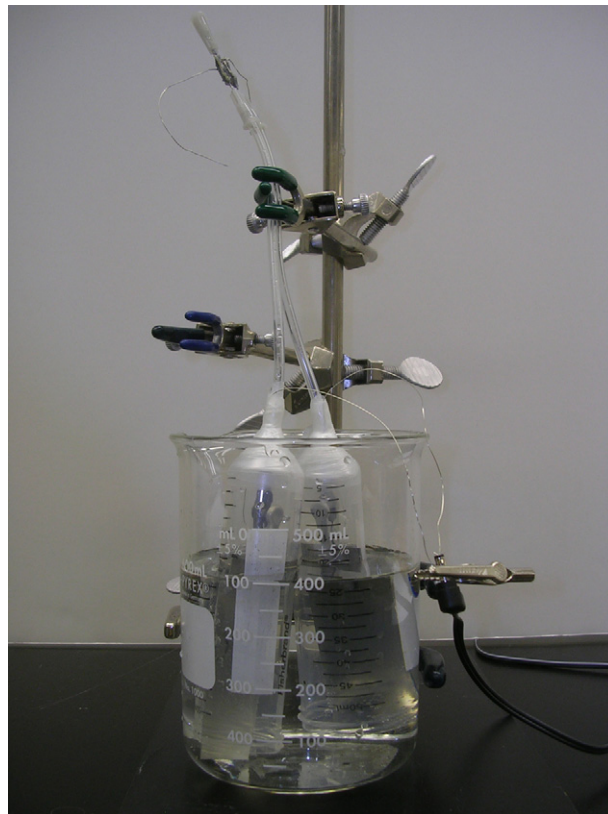


Fig. 13. A photo of the electrolyzer setup. A DC voltage source of 16.26 V was used.

tures above 2000 °C, Kapton® is converted into microcrystalline graphite [46]. Since, graphite is the material of choice for today's large fuel cells, we believe that pyrolyzed (and possibly graphitized) Kapton® can meet most of the specifications required for current and future fuel cells. The conductivity of graphitized Kapton® treated to temperatures exceeding 2000 °C is on the order of 10,000 S cm⁻¹ [44] and the conductivity of amorphous

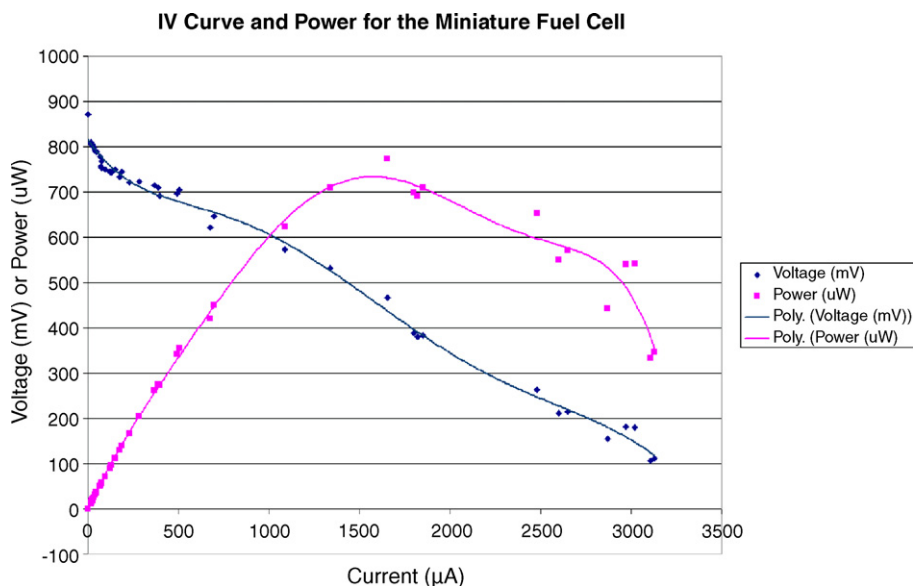


Fig. 12. The *I*–*V* curve and power of the fuel cell. The maximum power output is 0.773 mW.

carbon sheets made from pyrolyzing Kapton[®] at temperatures between 800 and 900 °C is on the order of 100 S cm⁻¹ [47,48]. Pyrolyzed Kapton[®] was found to be non-brittle in past literature [48]. The authors have also found pyrolyzed Kapton[®] to be non-brittle (see Section 1.5). Although pyrolyzed Kapton[®] sheets were found to be impervious [45], detailed permeability tests need to be performed.

One drawback of the use of polyimide is the high cost of the material. The raw material (Cirlex[®]/Kapton[®]) is currently expensive compared to other materials. For the thicknesses used in the prototype described above, the raw material cost per square inch is \$ 1.23. The material costs will, most likely, be the largest contributor to the entire cost of the bipolar plate if mass manufactured. It is difficult to estimate the cost of Cirlex[®] when subjected to economies of scale. The authors believe that the machining and heat treatment costs can be reduced by batch or continuous fabrication and/or by using more manufacturing-friendly techniques such as embossing.

4. Conclusions

A miniature fuel cell has been fabricated using a novel fluidic plate made by pyrolysis of machined polyimide. Epoxy sealing has been used to seal the fuel cell and a water management technique of exposing the Nafion[®] membrane has been used. To the best of our knowledge, the fuel cell prototype presented in this contribution is the world's smallest PEM fuel cell that utilizes carbon fluidics. Initial results have been presented. Further characterization of the fuel cell will be needed as well as testing of the water management method proposed. New prototypes using bipolar carbon plates arranged in a stack configuration will be fabricated and tested in future experiments.

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