Performance characteristics of a novel tubular-shaped passive direct methanol fuel cell

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ABSTRACT

The present work consists of a tubular-shaped direct methanol fuel cell (DMFC) that is operated completely passively with methanol solution stored in a central fuel reservoir. The benefit of a tubular-shaped DMFC over a planar-shaped DMFC is the higher instantaneous volumetric power energy density (power/volume) associated with the larger active area provided by the tubular geometry. Membrane electrode assemblies (MEAs) with identical compositions were installed in both tubular and planar-shaped, passive DMFCs and tested with 1, 2, and 3 M methanol solutions at room temperature. The peak power density for the tubular DMFC was 19.0 mW cm^{-2} and 24.5 mW cm^{-2} while the peak power density for the planar DMFC was 20.0 mW cm^{-2} and 23.0 mW cm^{-2} with Nafion® 212 and 115 MEAs, respectively. Even though the performance of the fuel cell improved with each increase in methanol concentration, the fuel and energy efficiencies decreased for both the tubular and planar geometries due to increased methanol crossover. The tubular DMFC experienced higher methanol crossover potentially due to a higher static fluid pressure in the anode fuel reservoir (AFR) caused by the vertical orientation of the tubular fuel reservoir. The performance of the tubular DMFC in this work represents an 870% improvement in power density from the previous best, passive, tubular DMFC found in the literature.
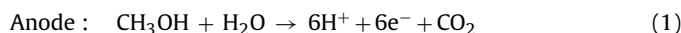
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1. Introduction

Recently, the direct methanol fuel cell (DMFC) has gained popularity in the fuel cell community as a potential candidate to replace lithium ion batteries in portable electronic applications. In addition to providing constant on-site power generation (unlike batteries, which require frequent recharging) the DMFC is known for its high energy density, compact configuration, low emissions, and low temperature operation. Unlike most fuel cells, the DMFC is unique, because it can be operated in active, semi-passive, and passive modes. During active operation, the DMFC produces maximum power but uses pumps, fans, heaters, and other auxiliary components to maintain the performance, which reduces the overall power output from the cell. Similarly, semi-passive operation also requires auxiliary components to maintain performance that subsequently reduce the overall power output from the cell. The goal of this work is to develop a completely passive, tubular DMFC that operates on its own without the assistance of extra components that require power and take up space, reducing the energy density of the fuel cell.
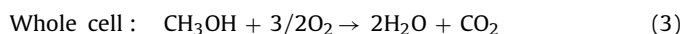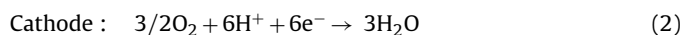
One of the most popular types of fuel cells, the PEM fuel cell, operates by performing reverse electrolysis, meaning that hydrogen and oxygen are combined to produce water, heat, and electricity. The DMFC is very similar to a basic PEM fuel cell, wherein methanol provides the hydrogen for the cell and oxygen is provided by the air. A DMFC can be broken into three main components: the anode, polymer electrolyte membrane, and cathode. At the anode, methanol diffuses through a porous gas diffusion layer (GDL) and oxidizes upon contact with the platinum–ruthenium (PtRu) catalyst to produce protons, electrons, and carbon dioxide. The polymer electrolyte membrane acts as a gas, liquid, and electrical insulator separating the anode and cathode sides, while allowing proton transport. At the cathode side, oxygen, provided by the external air surrounding the fuel cell, along with protons and electrons from the anode reaction is reduced upon contact with the platinum (Pt) catalyst produce electricity. In other words, a DMFC consists of a complete cycle broken into two reactions: one at the anode and one at the cathode. The methanol oxidation reaction (MOR) at the anode produces protons that transport through the polymer electrolyte membrane to the cathode and electrons that travel through an external circuit outside of the cell before returning to the cathode side to complete the oxygen reduction reaction (ORR). These reactions are further documented below. It is important to note that without either one of the anode or cathode reactions, the complete cell reaction would not occur and the fuel cell would not produce electricity.

$$\text{Anode}: \quad CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2 \tag{1}$$

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Cathode : $\quad 3/2O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ (2)

Whole cell : $\quad CH_3OH + 3/2O_2 \rightarrow 2H_2O + CO_2$ (3)

There have been extensive experimental research efforts discussing the development and subsequent improvement of passive, planar DMFCs [1–12]. One large problem hindering the commercialization of DMFCs is methanol crossover, which can be resolved by utilizing dilute methanol at the anode instead of high concentration or "neat" methanol. Dilute methanol has substantially less energy density compared to neat methanol since there is less fuel available to be used by the fuel cell. As a result, a larger anode fuel reservoir (AFR) is necessary to provide sufficient water to dilute the methanol fuel and prevent crossover, while also providing sufficient fuel to power the fuel cell. The DMFC has been considered a potential replacement for small, portable power applications, which means the final product (the fuel cell and AFR) must remain compact and capable of fitting in the current space occupied by Lithium Ion batteries. It is worthwhile to note that in passive DMFCs that are designed for portable applications, there is no additional fuel reservoir that accompanies the fuel cell. The fuel reservoir is built into the fuel cell assembly.

There have been very few experimental efforts towards the development of tubular-shaped DMFCs [13–21]. Table 1 provides a summary of the literature review of tubular-shaped DMFCs documenting the main important points from existing experimental efforts. Kunimatsu and Okada [13] fabricated a tubular DMFC that produced $12\,mW\,cm^{-2}$ during semi-passive operation. They injected an anode catalyst paste through a Flemion® tube, acting as the polymer electrolyte membrane, to a desired catalyst loading and painted a cathode catalyst layer onto the outside of the Flemion® tube with a spatula. A gold wire was used as a current collector on both sides of the membrane and 1 M methanol solution was injected through the tube during testing. They determined that the performance of the fuel cell is about six times higher for the case of a hot-pressed MEA.

Qiao et al. [14] further developed their tubular DMFC by applying the cathode catalyst layer onto the exterior of a Flemion® tube through the use of an impregnation-reduction technique. Once again, the anode catalyst was injected through the Flemion® tube to a desired loading and finally a maximum power density of $2\,mW\,cm^{-2}$ was produced during passive testing with 3 M methanol solution injected into the Flemion® tube. Qiao et al. [15] applied the impregnation reduction method to develop an anode catalyst layer on the inside of a Flemion® tube followed by subsequent half-cell testing. They further tested the DMFC [16] with the anode catalyst coating based on the impregnation-reduction method and the cathode catalyst coating painted onto the outside of the Flemion® tube with a spatula and produced a peak power density of $1.8\,mW\,cm^{-2}$ during passive DMFC testing conditions and with 2 M methanol solution.

Shao et al. [17] fabricated a tubular DMFC by coating the PtRu anode catalyst onto a titanium current collector. Next, a tubular-shaped titanium mesh, acting as the cathode current collector, was dipped into a carbon slurry, then dipped into a catalyst ink, and finally dipped a Nafion® solution producing a layer of each material on the porous, tubular-shaped titanium mesh. Finally, the anode catalyst-coated titanium mesh was spray-coated with Nafion® and wrapped around the cathode to create the total DMFC. Steady, long-term performance of the fuel cell was achieved during semi-passive operation in a liquid methanol bath and with air actively forced through the cathode. Shao et al. [18] further explained the results from their DMFC design indicating that they produced a maximum power density of $9\,mW\,cm^{-2}$ during semi-passive operation with 0.25 M methanol solution.

Yazici [19] designed and built a tubular fuel cell that could operate with hydrogen or methanol fuel at the anode and oxygen
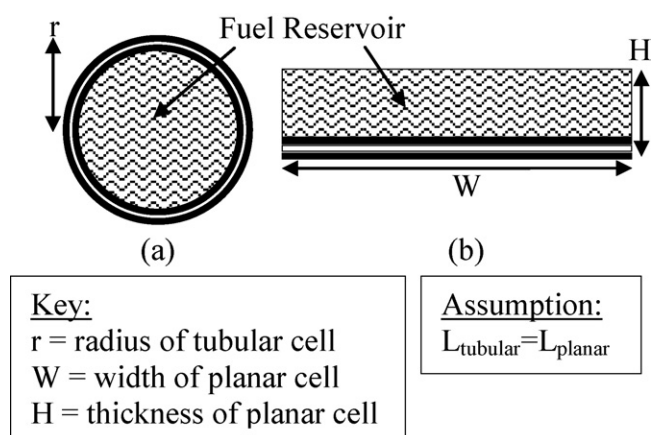

Fig. 1. Passive, DMFC schematics of two different geometries: (a) tubular and (b) planar.

passively provided by the air to the cathode. The layers of the fuel cell consisted of a central anode rod with machined channels, a mass transport layer (MTL) made from GRAFCELL porous graphite wrapped around the rod, a tubular-shaped Nafion® membrane slid onto the graphite MTL, another graphite MTL wrapped around the Nafion® membrane, and finally shrink tubing, with added holes to allow oxygen transport to the cathode. The shrink tubing helped to hold all the layers together and prevent leaking. This prototype was only tested with hydrogen and air semi-passively, but there was discussion that methanol could also be used instead of hydrogen at the anode. Yu et al. [20] developed an air-breathing, semi-passive, tubular-shaped fuel cell that produced $10\,mW\,cm^{-2}$ with 4 M methanol solution at $20\,mL\,min^{-1}$ and $60\,mW\,cm^{-2}$ with hydrogen gas supplied to the anode. They used a porous silica pipe that they injected perflourinated resin into as the polymer electrolyte membrane and measured the conductivity to be about eight times less than the proton conductivity of a Nafion® 115 membrane. Finally, Lee et al. [21] designed a tubular shaped apparatus enclosing planar MEAs connected in series.

A tubular-shaped DMFC has several advantages compared to a planar-shaped DMFC, namely:

- Ability to operate in all orientations without a lack of methanol contacting the anode catalyst layer (ACL).
- Reduced cost due to decreased volume of materials.
- Same shape as existing AA, AAA, D, and C batteries, which would allow easier conversion between batteries and fuel cells in the future.
- With the elimination of flow fields at the cathode, uniform pressure can be applied across the membrane electrode assembly (MEA).
- Under certain geometric conditions, a higher instantaneous volumetric power density associated with a higher power output per unit volume.

Energy density is defined as the total energy that a system can produce divided by the volume of the system while power density is defined as the power that a fuel cell can produce divided by the active area. In this work, a new term, instantaneous volumetric power density, is introduced which is defined as the instantaneous power that a fuel cell can produce divided by the total volume occupied by the fuel cell. The following simple analysis confirms that a tubular-shaped fuel cell can have a larger active area than a planar-shaped fuel cell for a given constant volume. The benefit of a larger active area is the higher instantaneous power that the fuel cell can generate.

Table 1
Literature review of tubular DMFC experimental efforts.

Investigator	Membrane	Anode/cathode locations[a]	Anode/cathode fuels	Operation	Performance	Comments
2004 – Kunimatsu et al. [13]	Flemion® tube	In/Out	1 M MeOH/air	Semi-passive	12 mW cm^{-2}	Good performance due to hot-pressing to keep layers of MEA together
2005 – Qiao et al. [14]	Flemion® tube	In/Out	2 M MeOH/air	Passive	2 mW cm^{-2}	Impregnation-Reduction method to coat CCL, poor performance
2005 – Qiao et al. [15]	Flemion® tube	In/NA	3 M MeOH/NA	Half-cell	NA	Impregnation-Reduction method to coat ACL, poor performance
2006 – Qiao et al. [16]	Flemion® tube	In/Out	2 M MeOH/air	Passive	1.8 mW cm^{-2}	Temperature treatment associated with impregnation-reduction method is harmful to membrane
2006 – Shao et al. [17]	Nafion® in Sol.	Out/In	MeOH/air	Active	NA	All layers are dipped or sprayed onto the fuel cell
2006 – Shao et al. [18]	Nafion® in Sol.	Out/In	0.25 M MeOH/air	Semi-passive	9 mW cm^{-2}	Good performance associated with conductive Titanium current collectors
2007 – Yazici [19]	Nafion® tube	In/Out	H$_2$/air	Semi-passive	NA	Good performance associated with shrink-tubing holding all MEA layers together, future DMFC testing with MeOH
2007 – Yu et al. [20]	Perfluorinated resin in porous silica tube	In/Out	4 M MeOH/air	Semi-passive	10 mW cm^{-2}	Used a frame design to hold the MEA layers together and prevent leakage, poor membrane conductivity compared to Nafion®
Present work	Nafion® 212 and 115 membranes	In/Out	1, 2, 3 M MeOH/air	Passive	24.5 mW cm^{-2}	Advantages: frame, Nafion® membrane, passive, stainless steel current collectors

[a] Inside the tubular DMFC (In) versus outside of the tubular DMFC (Out).

Considering both tubular and planar-shaped DMFCs, described in Fig. 1, that individually occupy the same volume, V_o, and assuming the length of the tubular cell to be equal to the length of the planar cell ($L_{tubular} = L_{planar}$), the radius of the tubular fuel cell, as a function of the height and width of the planar fuel cell, is:

$$r = \sqrt{\frac{HW}{\pi}} \qquad (4)$$

Assuming that the thickness of the MEA in a DMFC is approximately 0.75 mm, which is negligible in comparison to the thickness/radius of the liquid fuel reservoir due to orders of magnitude (>10 mm), the ratio of the tubular active area to the planar active area is represented by:

$$\frac{A_{tubular}}{A_{planar}} = \frac{2\pi r L_{tubular}}{W L_{planar}} \qquad (5)$$

Plugging Eq. (4) into Eq. (5) produces a relationship that represents the ratio of the tubular active area to the planar active area as:

$$\frac{A_{tubular}}{A_{planar}} = 2\sqrt{\pi}\left(\sqrt{\frac{H}{W}}\right) \qquad (6)$$

From Eq. (6), it can be concluded that the active area of a tubular-shaped DMFC will be larger than the active area of a planar-shaped DMFC as long as the relationship between the width and height of a planar-shaped DMFC is:

$$\frac{W}{H} < 4\pi \qquad (7)$$

In real, portable, small-scale applications, the ratio of the width to the height in a passive DMFC is usually less than 4π. Thus, the tubular-shaped, passive DMFC would prove to be beneficial for high power, small-scale, portable applications.

Considering the limited experimental work documented in Table 1, a novel passive, tubular-shaped DMFC frame was designed and fabricated to hold the MEA layers together more effectively, prevent leakage, and reduce the internal resistance across the fuel cell. The frame also provides channels for passive air-breathing to the cathode and an AFR to hold methanol in the center of the frame. Two different conventional MEAs, one with a Nafion® 212 membrane and the other with a Nafion® 115 membrane, were installed in the tubular frame and the DMFC was tested with 1 M, 2 M, and 3 M methanol solutions completely passively. Polarization curves were generated for each methanol concentration and constant voltage tests were run to determine both the fuel and energy efficiencies. The results from the tubular-shaped DMFC tests were also compared with identical tests run on a passive, planar-shaped DMFC using identical MEAs. The proposed tubular-shaped, passively operated DMFC shows significant improvement over existing tubular-shaped DMFCs reported in the literature.

2. Experimental

2.1. Membrane electrode assembly

Fig. 2 shows a schematic diagram of the proposed tubular-shaped, passive DMFC. Fig. 2(a) includes a labeled diagram of the MEA. The MEA consists of a custom-designed CCM sandwiched between two GDLs. The CCM is made from both Nafion® 212 and 115 polymer electrolyte membranes coated with 5 mg cm^{-2} PtRu as an anode catalyst layer and 5 mg cm^{-2} Pt as a cathode catalyst layer from BCS Fuel Cells, Inc. in Texas. Considering the performance of previous tubular experimental efforts [13–21], a Nafion® membrane was chosen as the optimal material to use as a polymer electrolyte layer in the fuel cell over the Flemion® tube [13–18] and the perfluorinated resin injected into the porous sil-
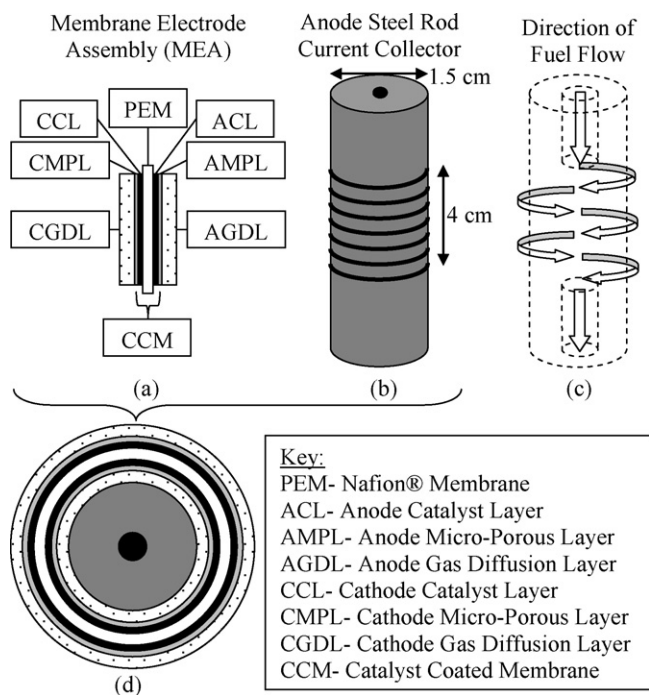
Fig. 2. Diagram of the tubular-shaped DMFC, describing the (a) layers of the MEA, (b) anode current collector rod, (c) direction of fuel flow through the anode current collector, and (d) MEA wrapped around the inner steel rod current collector.

ica pipe [20] based on low methanol crossover and high proton conductivity.

The CCM had to be custom designed so that it would fit into the tubular-shaped frame that had been designed and fabricated specifically for this experiment. The tubular CCM design included a 6 cm × 6 cm Nafion® membrane with two different sized catalyst coated areas: the anode with a 4 cm × 5.3 cm catalyst area and the cathode with a 4 cm × 5.6 cm catalyst area. Since the CCM is wrapped around a steel rod during installation into the tubular-shaped DMFC frame, the actual area of the inner anode catalyst surface is smaller than the area of the external, cathode catalyst surface due to different radii as shown in Figs. 1(a) and 2(d). As a result, the tubular frame had to be designed, built, and tested to assure that the fuel cell would operate accordingly before the CCMs were designed and fabricated.

The area of the anode catalyst surface was estimated based on the circumferential area of the steel rod, with area added to account for expansion and contraction of the Nafion® membrane as it absorbs and expels water or methanol during testing. Covering both the anode and cathode catalyst layers, the GDLs are made from 50% PTFE wet-proofed carbon cloth from clean fuel cell energy with a 4.6 mg cm^{-2} micro-porous layer (MPL) loading coated in-house. The composition of the MPL is 25% Nafion® ionomer (Dupont 5% Nafion® solution, 1100EW) and 75% carbon powder (Cabot brand Vulcan XC72R, GP-3860). MPL ink is produced by combining the Nafion® solution, carbon powder, and ethanol (as a solvent), then sonicating the solution for 30 min and applying the ink to the GDL via the "straight edge" technique. The "straight edge" technique includes using a dropper to add MPL ink directly onto the carbon cloth followed by using a flat, smooth edge (from a piece of metal, ruler, scraper, etc.) to evenly distribute the ink across the GDL. Following each application of ink to the GDL, the carbon cloth is left to dry, weighed, and repeated as necessary to achieve the desired MPL loading. Finally, the GDL is placed in an oven at 350 °C to sinter the carbon particles. The purpose of the MPL is to increase the mass transport resistance through the diffusion layer, to protect the catalyst layer, and also to add additional insulation to

maintain an optimal cell temperature. The GDLs are sandwiched around the CCM with the MPLs in contact with each catalyst layer.

Prior to testing, the MEA is not hot-pressed. Instead, the MEA is pressed between two graphite current collectors in a 5 cm × 5 cm, planar, active fuel cell frame, which helps to press the three layers of the MEA together. The frame is heated to 80 °C while 80 °C distilled water is fed through the anode channels and 100% humidified air at 80 °C is fed through the cathode channels. The goal of this step, the hydration process, is to completely saturate the Nafion® membrane with water, which in turn reduces the internal resistance of the fuel cell by improving the proton conductivity of the membrane. This process is completed once the resistance across the MEA reduces to less than 15 mΩ (approximately 2 h). Next, the MEA is activated by applying a constant voltage (0.6 V) load to the cell until a steady current density is produced from the fuel cell. First, the fuel cell frame is heated to 80 °C while 100% humidified hydrogen is fed through the anode channels at 0.8 L min^{-1} and 100% humidified oxygen is fed through the cathode channels at 0.4 L min^{-1}.

After obtaining a steady current density from the fuel cell, a performance test is conducted to produce a polarization curve for the fuel cell during hydrogen and oxygen testing to compare against the performance from other MEAs. Next, the cell is cooled to 60 °C and dilute methanol (~1 M) is fed through the anode channel at 1 mL min^{-1} while room temperature air is fed through the cathode channel at 0.3 L min^{-1}. Again, a constant voltage (0.3 V) load is applied to the cell until a steady current density is produced and another performance test is run to produce a polarization curve for methanol and air. Finally, upon completion of the methanol and air testing, the active fuel cell frame is cooled to room temperature and the MEA is removed and installed into the tubular-shaped DMFC frame.

2.2. Tubular cell fixture

Considering the popularly used planar, passive DMFC structure, a tubular, passive DMFC frame was custom designed and fabricated to improve upon the existing performance of tubular DMFCs. The purpose of designing a passive, tubular-shaped DMFC frame is:

- To recreate testing conditions similar to those of the planar, passive DMFC, which has proven successful performance associated with a frame that houses the MEA.
- To provide sufficient, uniform, pressure across the MEA layers in order to reduce the overall internal resistance.
- To provide a strong central rod to wrap the MEA around, act as a current collector, and provide channels to transport methanol fuel to the anode side of the fuel cell.
- To provide an external current collector around the MEA with machined channels that allow sufficient passive air flow to the cathode side of the fuel cell.
- To provide insulation for the fuel cell to improve the kinetics at each catalyst layer.

The frame was initially fabricated from carbon, for conductive purposes, but later was rebuilt from stainless steel to account for structural strength. The electrical conductivity of stainless steel is slightly lower than that of carbon, but stainless steel has been used as a current collector in previous passive DMFC research because of its strength, resistance to corrosion, and good conductivity. Figs. 2(b) and 3(a) show the stainless steel rod that the MEA is wrapped around during installation. This rod acts as the anode current collector and also has a fuel channel machined in a helix pattern around the outside of the rod to allow methanol transport. Fig. 2(c) shows the direction of methanol flow first axially
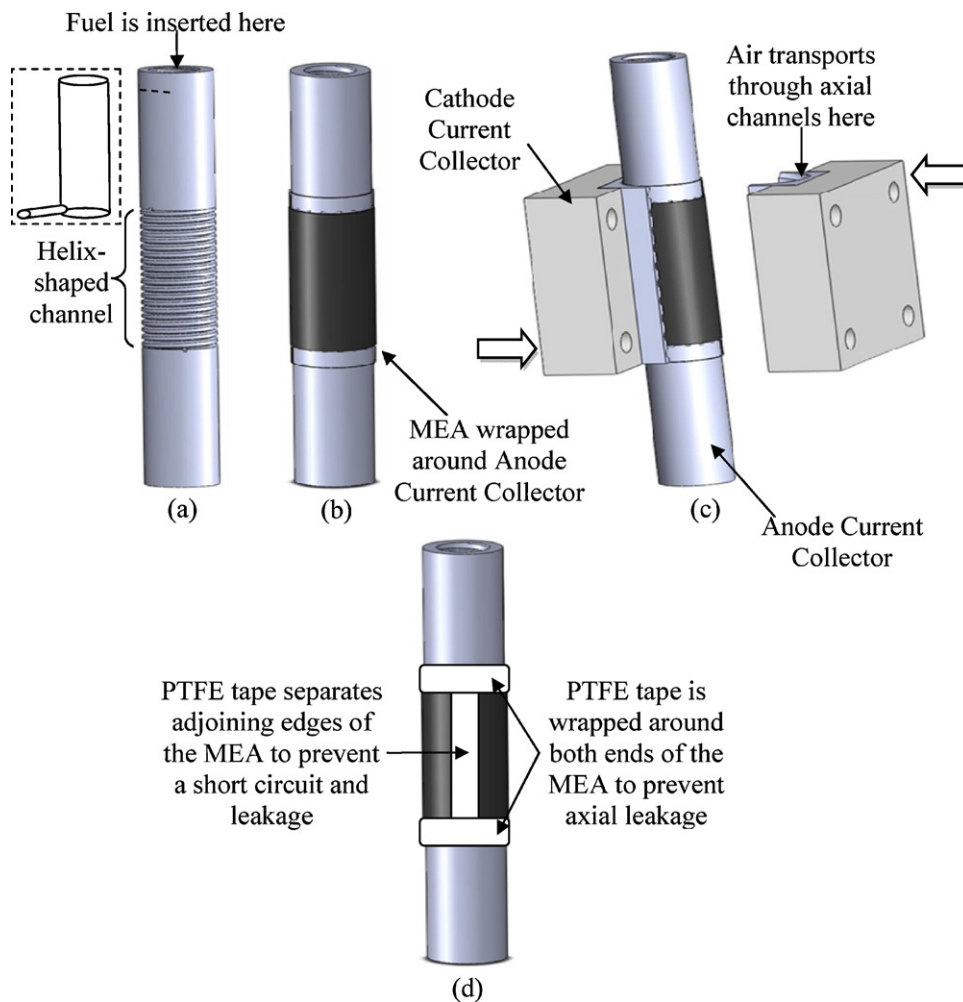
Fig. 3. Schematic showing the steps to build the fuel cell frame including the (a) anode current collector rod with helix-shaped fuel channel, (b) MEA wrapped around the helix-shaped fuel channel, (c) cathode current collector enclosing the MEA and anode current collector, and (d) three locations of PTFE tape.

through the center of the rod, then the methanol flows out of the center of the rod to the exterior of the rod and radially around the helix-shaped channel, and finally it returns to the center of the rod and exits axially out the bottom of the rod. During installation, the activated MEA is wrapped around the rod, with the anode gas diffusion layer in contact with the rod and covering the helix shaped fuel channel. The two adjoining edges of the MEA are separated by a piece of polytetrafluoroethylene (PTFE) tape. PTFE tape is also wrapped around either end of the MEA. The three locations of PTFE tape are described further in Fig. 3(d). The PTFE tape is used because:

- It creates a leak-proof seal along the adjoining edges of the MEA.
- It prevents the anode and cathode GDLs from touching and causing a short circuit.
- It is a good non-conductive, insulating, sticky material.

The total active area of the MEA is calculated based on the total surface area in contact between the anode GDL and the anode stainless steel rod. It is simply the surface area of the stainless steel rod in the region of the fuel channels minus the area of the piece of PTFE tape that connects the adjoining edges of the MEA. Using the dimensions shown in Fig. 2(b) and subtracting the area of the PTFE tape between the adjoining edges of the MEA, the total active area for the MEA is 13.77 cm^2.

The entire tubular fuel cell frame consists of three pieces: the inner stainless steel rod, which is used as the anode current collector, and an outer cathode current collector that is broken into two pieces. The outer part of the frame is also made from stainless steel and acts as the cathode current collector. In order to clamp down around the MEA, the outer section is designed as two pieces that fit together on opposite sides of the anode rod, around the MEA. Fig. 3 shows a breakdown of the steps taken to construct the tubular fuel cell frame enclosing the MEA. The diameter of the inner anode steel rod is 1.5 cm and the diameter of the external steel portion of the frame that closes around the MEA and anode steel rod is 1.6 cm. Considering an average DMFC MEA to be 0.075 cm thick, this provides 0.05 cm between the inner anode steel rod and the exterior cathode current collector so that pressure is applied across the MEA layers as the outer cathode portion of the frame closes around the MEA.

Longitudinal air flow channels are machined into the cathode current collector pieces to allow sufficient passive air flow from the external ambient air to the cathode side of the fuel cell. The air flow channels are 5 mm deep, 2 mm wide, and travel the entire length of the frame to allow air entry or exit from either side of the frame. The outer portion of the fuel cell frame serves several purposes, including:

- Providing uniform pressure across the MEA to reduce the internal resistance.

- Acting as a current collector for the cathode side of the fuel cell.
- Providing channels for passive air transport to the cathode side of the fuel cell.
- Insulating the MEA to maintain a temperature higher than the ambient air, to improve the kinetics at each catalyst layer.
- Providing protection from external debris and dust that could hinder the performance of the fuel cell.

2.3. Testing procedure

Once the MEA is installed into the tubular fuel cell frame, water is passed through the anode fuel channels to check for liquid-leaks. During the initial design/testing stages; leaks were a frequent problem associated with the tubular frame design, since there were three different locations that leaked fluid: the adjoining edges of the MEA when it is wrapped around the anode rod, and both ends of the MEA. Careful, meticulous installation of the MEA into the tubular frame and PTFE tape added between the adjoining edges of the MEA and wrapped around both ends of the MEA helped to prevent leaks. It is important to prevent leaks and install the MEA correctly during the first installation to prevent degradation of the MEA caused by excessive contact and flexing of the MEA layers during repeated reinstallations.

A Multi Range Fuel Cell Test System from Scribner Associates (850e) was used to test the fuel cell by applying an adjustable, electronic load along the circuit connecting the anode and cathode. Anode and cathode electrical leads were connected to the central steel rod and exterior steel portion of the frame, respectively, to apply the load across the cell. The tubular DMFC was tested with 1 M, 2 M, and 3 M methanol solutions, since higher concentrations of methanol would result in methanol crossover and subsequent damage to the MEA due to de-lamination of the layers. Before the start of each test, methanol solution was injected into the AFR until the entire fuel channel was filled. During all of the tests, the fuel cell was operated with the anode steel rod pointing upward while the bottom of the rod was taped to hold the methanol solution in the rod during operation. The tape was removed upon the completion of each test to allow any excess fuel and water to drain from the AFR. Another reason that the steel rod was positioned vertically during testing was to allow generated carbon dioxide gas to escape through the AFR due to buoyancy forces. In between tests, air was forced through the anode fuel channel to remove all the liquid and carbon dioxide from the previous test. The fuel cell was stored overnight with distilled water in the AFR to maintain the water content in the membrane and to assure consistent performance the next day. Long-term, constant voltage tests and polarization curves were performed for each concentration of methanol to validate the long-term performance of the fuel cell and to calculate the fuel and energy efficiencies of the tubular DMFC during completely passive operation. The polarization curves were measured after each fuel cell had achieved a steady open circuit voltage following each new addition of methanol into the fuel cell reservoirs. A thermocouple was installed at the cathode side of the MEA, in the air channel contacting the GDL, to measure the temperature of the fuel cell during operation.

To perform a long-term constant voltage test, 2 mL of methanol solution was initially injected into the AFR. Next, a constant 0.35 V load was applied to the cell and the corresponding current density versus time was recorded until the cell had used up all of the methanol in the fuel reservoir and the current density reduced to zero. Considering the results from the long-term constant voltage tests for each methanol concentration, both the fuel and energy efficiencies of the DMFC with Nafion® 212 and Nafion® 115 membranes were calculated and compared with the fuel and energy efficiencies of a planar-shaped DMFC, also operated passively. The fuel efficiency is calculated by comparing the total current pro-

duced by the fuel cell to the actual total current that the fuel cell should produce based on a given volume of fuel [5]. This is represented by the following equation:

$$\eta_{\text{fuel}} = \frac{\int_0^t i(t)\,dt}{6 C_m V_m F} \times 100 \tag{8}$$

where $i(t)$ is the current produced by the fuel cell at a given time t integrated over the total time of the test, C_m is the concentration of methanol used in the cell, V_m is the volume of methanol injected into the anode fuel cell, and F is Faraday's Constant (96485 C mole^{-1}). The energy efficiency compares how much power the fuel cell produced to how much power is actually available in a given volume of fuel [5], and is represented by the following equation:

$$\eta_{\text{energy}} = \frac{V \int_0^t i(t)\,dt}{6 C_m V_m F V_o} \times 100 \tag{9}$$

where V is the operating voltage of the fuel cell (0.35 V) and V_o is the maximum cell voltage considering no irreversibilities (1.18 V).

A passive, planar DMFC with a 3 cm × 3 cm active area was also tested with identical Nafion® 212 and 115 CCMs from BCS Fuel Cells, Inc. with the same 5 mg cm^{-2} anode and cathode catalyst loadings. Similarly to the tubular DMFC, the planar DMFC was tested with 1 M, 2 M, and 3 M methanol solutions in identical conditions (room temperature, passive) to produce comparable results. To account for similar constant voltage experiment run times, unlike the tubular DMFC which was tested with 2 mL of methanol, the planar DMFC was tested with 1.3 mL of methanol. This volume was calculated by setting the ratio of fuel volume to active area for the tubular DMFC equal to the ratio of volume to active area for the planar DMFC. Table 2 provides a comparison summarizing of the performance results from the planar and tubular passive, DMFCs.

3. Results and discussion

3.1. Performance

Fig. 4 represents the performance of the tubular DMFC during passive operation with 1 M, 2 M, and 3 M methanol solutions, respectively. Prior to each test, new methanol solution was injected into the AFR. Oxygen was provided by the air to the cathode side of the fuel cell. For both the Nafion® 212 and 115 MEAs, the performance of the tubular DMFC improved with each increase in methanol solution due to an increased methanol concentration at the ACL/Nafion® membrane interface. For example, the peak power density of the tubular DMFC increased from 10.6 to 19.0 mW cm^{-2} and from 15.3 to 24.5 mW cm^{-2} as the methanol concentration increased from 1 M to 3 M with the Nafion® 212 and 115 MEAs, respectively. With a larger concentration of fuel available at the ACL/Nafion® membrane interface, the anode irreversibilities were reduced, and as a result, the cell performance was improved. However, with a higher concentration of methanol, there is a higher quantity of methanol crossover from the anode to the cathode. Crossover methanol that reacts at the cathode side of the fuel cell produces large amounts of heat which, as a result, increases the temperature of the fuel cell. Methanol crossover ultimately results in decreased fuel efficiency, but an increase in cell temperature improves the kinetics at both the anode and cathode catalyst layers and, thus, the performance of the fuel cell.

The performance of the tubular DMFC is better with the Nafion® 115 MEA than with the Nafion® 212 MEA for all methanol concentrations. For the Nafion® 212 MEA, the maximum power densities were 10.6, 14.5, and 19.0 mW cm^{-2} with 1 M, 2 M, and 3 M methanol solutions, respectively. For the Nafion® 115 MEA,

Table 2
Comparison of planar and tubular, passive DMFCs.

| DMFC type	Nafion® membrane	[MeOH] (mole L^{-1})	Maximum power density (mW cm^{-2})	Limiting current density (mA cm^{-2})	Maximum temperature change (°C)[a]
Planar	212	1.0	8.3	25.7	1
		2.0	13.9	58.9	1
		3.0	20.0	124.1	3
	115	1.0	9.8	27.2	1
		2.0	20.2	59.9	2
		3.0	23.2	126.3	2
Tubular	212	1.0	10.6	42.5	1
		2.0	14.5	63.3	2
		3.0	19.0	115	3
	115	1.0	15.3	60.1	0
		2.0	19.4	90.4	1
		3.0	24.5	136	2

[a] During constant voltage discharge at 0.35 V.

the maximum power densities were 15.3, 19.4, and 24.5 mW cm^{-2} with 1 M, 2 M, and 3 M methanol solutions, respectively. A Nafion® 212 membrane is thinner and has a lower resistance to proton conductivity but will allow more methanol crossover. A Nafion® 115 membrane is thicker and has a higher resistance to proton conductivity, but will provide better resistance to methanol crossover than the Nafion® 212 membrane.

The main reason that the Nafion® 115 MEA performed better than the Nafion® 212 MEA was that the Nafion® 115 MEA allowed the fuel cell to achieve a much higher limiting current density for each corresponding voltage due to its resistance to methanol crossover. For the 3 M methanol solution case, the Nafion® 115 MEA's limiting current density was 136 mA cm^{-2} while that of the Nafion® 212 MEA was 115 mA cm^{-2}. For the 2 M methanol solution case, the Nafion® 115 MEA's limiting current density was 90.4 mA cm^{-2} while that of the Nafion® 212 MEA was 63.3 mA cm^{-2}. For the 1 M methanol solution case, the Nafion® 115 MEA's limiting current density was 60.1 mA cm^{-2} while that of the Nafion® 212 MEA was 42.5 mA cm^{-2}. Both the Nafion® 212 and 115 CCMs were custom made for these experiments; thus, another potential reason for the varied performance between these two

membranes is fabrication error, which was initially seen by the non-uniform catalyst layer on the Nafion® 212 CCMs.

Identical tests were run with the planar DMFC to generate polarization curves for the same Nafion® 212 and 115 MEAs. Fig. 5 represents the performance of the planar DMFC during passive operation with 1 M, 2 M, and 3 M methanol solutions, respectively. By comparing the peak performance, limiting current densities, and range of voltage for the tubular and planar geometries shown in Fig. 4 and Table 2, it is apparent that the tubular DMFC performed better than the planar DMFC. The tubular DMFC produced a higher power density than the planar DMFC for every methanol concentration using both Nafion® 212 and 115 MEAs. For example, the peak power density was 24.5 mW cm^{-2} for the tubular DMFC and 23.2 mW cm^{-2} for the planar DMFC operating with a Nafion® 115 membrane and 3 M methanol solution. The tubular DMFC also produced a higher limiting current density than the planar DMFC for every methanol concentration and with both Nafion® 212 and 115 MEAs except for the Nafion® 212 MEA with 3 M methanol solution. The higher power density associated with the tubular DMFC compared to the planar DMFC can be attributed to the large constant pressure applied across the MEA, as well as, a higher tempera-
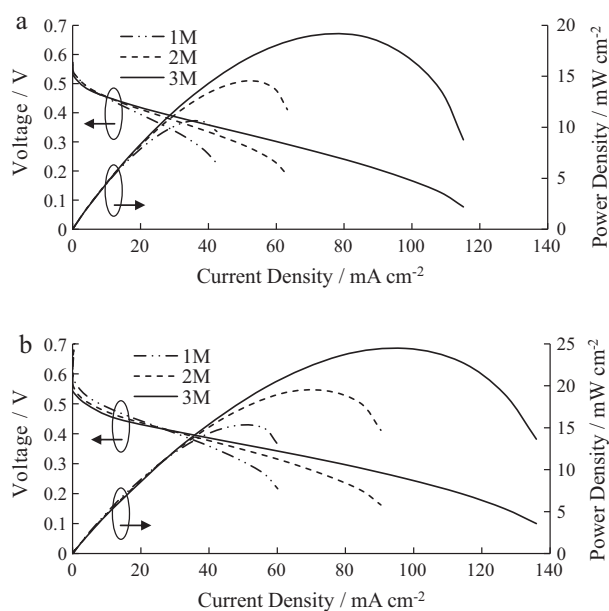
Fig. 4. Passive, tubular DMFC polarization curves for 1, 2, and 3 M methanol solutions utilizing (a) a Nafion® 212 CCM and (b) a Nafion® 115 CCM.
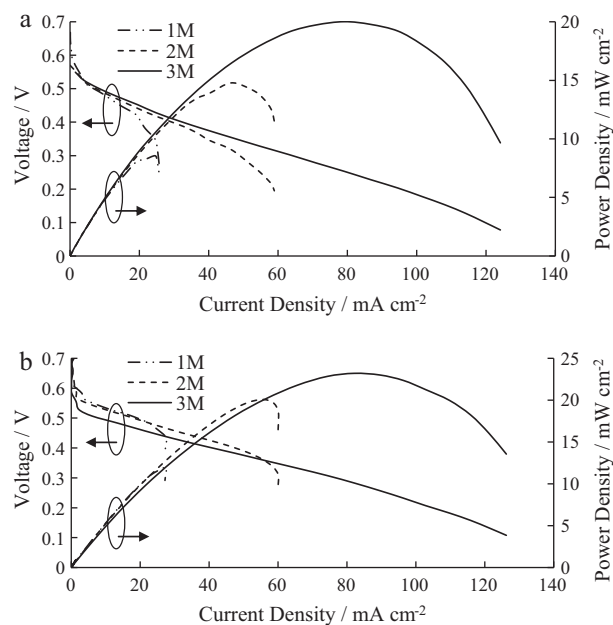
Fig. 5. Passive, planar DMFC polarization curves for 1, 2, and 3 M methanol solutions utilizing (a) a Nafion® 212 CCM and (b) a Nafion® 115 CCM.
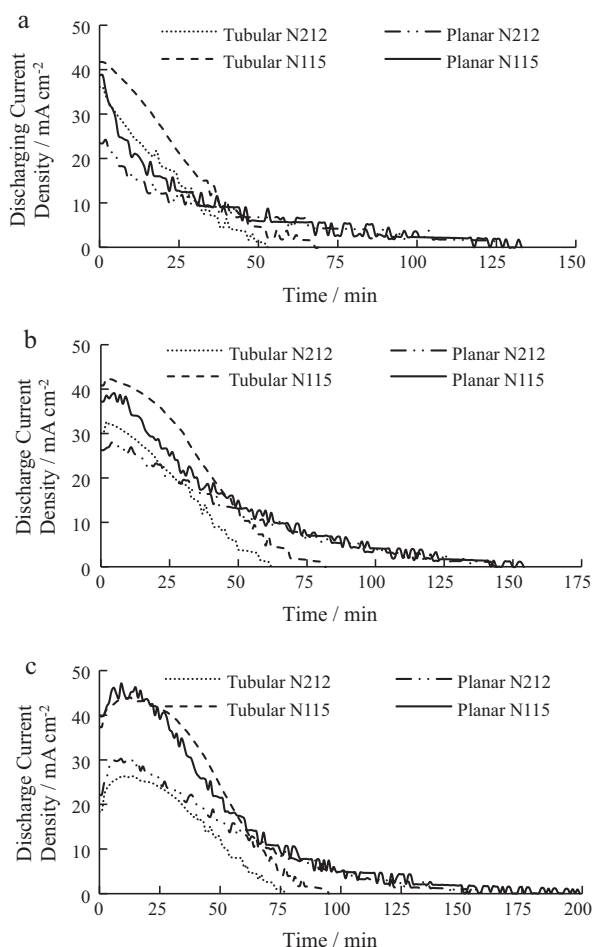
Fig. 6. Variation of tubular and planar constant voltage (0.35 V) discharge current density versus time with Nafion® 212 and 115 MEAs utilizing (a) 1 M (b) 2 M and (c) 3 M methanol solutions.

ture rise in the tubular cell associated with increased methanol crossover.

These results are very promising, since they show a significant improvement in performance for the passive, tubular DMFC. Based on the literature review, shown in Table 1, the previous best passive, tubular DMFC performance was 2 mW cm⁻² with 2 M methanol solution [15] and the best semi-passive, tubular DMFC performance was 12 mW cm⁻² with 1 M methanol solution [14]. In this work, a passive, tubular DMFC was designed and fabricated that produced 19.4 mW cm⁻² with 2 M methanol solution and 15.3 mW cm⁻² with 1 M methanol solution, which shows an 870% improvement in power from the previous passive, tubular DMFC and a 27.5% improvement in power from the semi-passive, tubular DMFC. If the existing tubular DMFC is tested in a semi-passive mode, it should produce a much higher peak power density and limiting current density.

3.2. Constant voltage discharge

Fig. 6 presents the results from the constant voltage (0.35 V) tests with the tubular and planar DMFCs, respectively. Initially, 2 mL of methanol solution was injected into the AFR and the corresponding current density versus time was recorded and displayed in the figures. For each concentration of methanol, the planar DMFC operated for a longer period of time than the tubular DMFC. The results in Fig. 6 for the tubular DMFC all show a linear relationship between the discharging current density and time while the

curves representing the planar DMFC follow more of an exponential decay.

Unlike the planar geometry, which has methanol resting on top of the MEA, the liquid methanol in the tubular DMFC is positioned in a vertical fuel channel then a helix-shaped channel, then another vertical channel at the bottom of the anode current collector. The tubular DMFC was tested with the anode rod positioned vertically to allow generated carbon dioxide gas to escape through the top of the rod. The vertical alignment of the tubular DMFC actually caused an increased methanol crossover with time due to a higher static fluid pressure in the tubular DMFC than in the planar DMFC. The height of the liquid methanol fuel in the planar AFR was less than 5 mm while the height of the fuel in the tubular AFR was 8 cm (height of the helix shaped channel plus the height of the central channel in the anode rod above the helix-shaped channel). Thus, the static fluid pressure at the bottom of the tubular DMFC is larger than the static fluid pressure in the planar DMFC which explains why the curves for the planar and tubular current density discharges in Fig. 6 are different shapes.

With an increased static fluid pressure, the rate of methanol crossover in the tubular DMFC increased due to large pressure gradients across the Nafion® membrane. This explains why the discharging current density decreased to zero faster in the tubular DMFC than in the planar DMFC, because there was more fuel lost in the tubular DMFC. It is worthwhile to note that the tubular DMFC produced an initial discharging current density similar to that of the planar DMFC, for all methanol concentrations, which reinforces the assertion that the tubular and planar DMFCs perform similarly. The main difference between the tubular and planar results, shown in Fig. 6, was that the tubular DMFC experienced significantly higher methanol crossover than the planar DMFC, which can be attributed to a higher static fluid pressure in the AFR.

The constant voltage discharge experiments with the Nafion® 115 MEA operated for a longer period of time than those with the Nafion® 212 MEA due to decreased methanol crossover associated with the thicker membrane. As the methanol is lost due to crossover, there is less fuel available, so the DMFC operates for a shorter period of time. The discharging current density for both the tubular and planar DMFCs was higher for the tests with the Nafion® 115 MEA than the tests with the Nafion® 212 MEA, once again due to decreased methanol crossover which produces higher performance from the fuel cell.

The tubular DMFC initially had a higher discharging current density than the planar DMFC for both Nafion® 212 and 115 MEA cases with 1 M and 2 M methanol solution, but during the 3 M methanol testing the planar geometry produced a higher initial discharging current density. One explanation for this is the geometry of the fuel cell. During construction of the tubular DMFC, an MEA is activated in a planar frame then wrapped around the central tubular rod which could induce stress fractures (cracks) in the MPL material initially applied and dried onto the GDL, and reduce the mass transport resistance of the MPL. Another explanation for the decreased discharging current density associated with the tubular DMFC and 3 M methanol solution is the increase in methanol crossover with an increase in methanol concentration. It is worthwhile to note that the methanol crossover also increased in the planar DMFC as the concentration of methanol increased, but at a smaller rate than in the tubular DMFC. There are several other factors that could affect the methanol crossover in the tubular-shaped fuel cell compared to the planar-shaped fuel cell, including the possible differences in water crossover and liquid saturation at the catalyst layers for two geometries [22–24]. It should be noted that the higher static fluid pressure is only one potential explanation for the higher methanol crossover in the tubular-shaped fuel cell. Further research is required to fully understand the phenomenon affecting methanol crossover due to a change in geometry.
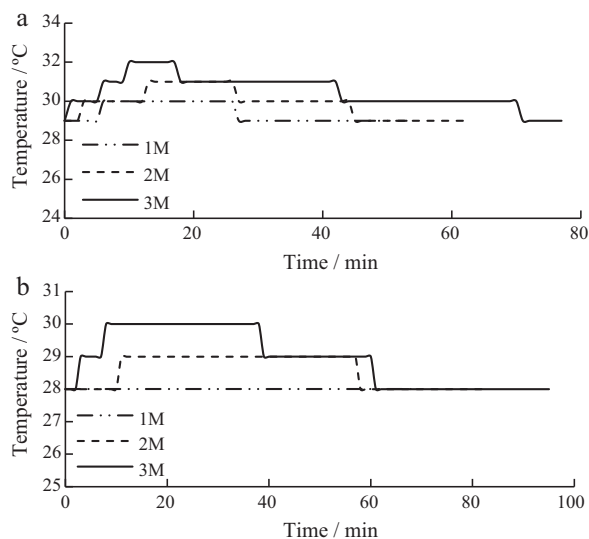
Fig. 7. Tubular temperature profile during constant voltage discharge experiment with (a) a Nafion® 212 CCM and (b) a Nafion® 115 CCM.

Fig. 8. Comparing the (a) fuel efficiency and (b) energy efficiency of the Nafion® 212 and 115 membranes in the tubular-shaped and planar-shaped DMFCs operated passively with 1, 2, and 3 M methanol solutions.

Fig. 7 presents the temperature of the tubular DMFC during the constant voltage discharge experiments starting from ambient temperature for each case. Due to an increased methanol crossover during testing with the Nafion® 212 MEA, the temperature increases for all methanol concentrations are higher during the constant voltage tests with the Nafion® 212 MEA than with the Nafion® 115 MEA. As methanol crosses over the membrane, it reacts at the cathode catalyst layer causing an increase in the cell temperature and also reducing the overall cell current density as reflected in Fig. 6, with the Nafion® 212 MEA discharges producing lower current density than the Nafion® 115 MEA discharges. It is also worthwhile to note that during the tubular DMFC constant discharge experiments that the change in cell temperature increased as the concentration of methanol increased. Operation with 3 M methanol solution produced a temperature change of 3 °C and 2 °C with Nafion® 212 and 115 MEAs, respectively, while operation with 1 M only produced a change of 1 °C and 0 °C with the Nafion® 212 and 115 MEAs, respectively.

3.3. Efficiency

Following each constant voltage test, both the fuel and energy efficiencies of the tubular and planar DMFCs were calculated using Eqs. (8) and (9). Fig. 8 presents the resulting fuel and energy efficiencies of the tubular and planar DMFCs with the Nafion® 212 and 115 MEAs, respectively. For both the tubular and planar DMFCs, the fuel and energy efficiencies are the greatest during operation with 1 M methanol solution and the least during operation with 3 M methanol solution due to methanol crossover that results in lost fuel and subsequently less available energy. For example, the fuel efficiency for the tubular DMFC with the Nafion® 212 MEA decreased from 62.6% to 41.6% to 32.0% as the methanol concentration increased from 1 M, to 2 M, to 3 M. During operation with 1 M methanol solution, the least fuel crosses over both the Nafion® 212 and 115 membranes and is instead utilized at the anode to produce power, but as the methanol concentration increases, the quantity of methanol crossover also increases and the efficiency decreases.

For both the tubular and planar DMFCs, the fuel and energy efficiencies increase substantially for the Nafion® 115 MEA compared to the Nafion® 212 MEA. In the case of the tubular DMFC, the fuel efficiency for the Nafion® 212 MEA was 62.6%, 41.6%, and 32.0%
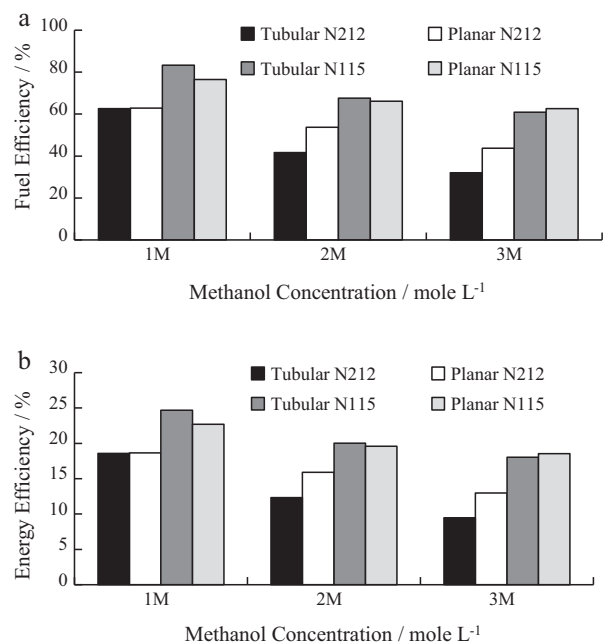
with 1 M, 2 M, and 3 M methanol solutions, respectively. However during operation with the Nafion® 115 MEA, the fuel efficiency for the tubular DMFC increased to 83.3%, 67.6%, and 60.8% with 1 M, 2 M, and 3 M methanol solutions, respectively. Similarly to the fuel efficiency, the energy efficiency for the tubular DMFC decreased from 18.6%, to 12.3%, to 9.5% with the Nafion® 212 MEA and from 24.7%, to 20.0%, to 18.0% with the Nafion® 115 MEA during 1 M, 2 M, and 3 M operation, respectively.

Even though the fuel and energy efficiencies for both the tubular and planar DMFCs decrease as the methanol concentration increases, it is worthwhile to note that the difference between the fuel and energy efficiencies of the planar and tubular DMFCs increase significantly during 2 M and 3 M methanol solution operation and with the Nafion® 212 MEA. Initially, with the 1 M methanol solution, both the fuel and energy efficiencies of the tubular DMFC are similar to the fuel and energy efficiencies of the planar DMFC with the Nafion® 212 MEA, but as the methanol concentration increases to 2 M and then 3 M, the efficiencies of the planar DMFC become higher than the efficiencies of the tubular DMFC. For example, the fuel efficiency with the Nafion® 212 MEA decreased from 63.9%, to 53.7%, to 43.7% for the planar DMFC, while the fuel efficiency for the tubular DMFC decreased from 62.6%, to 41.6%, to 32.0%. The difference between the planar and tubular fuel efficiency increases as the methanol concentration increases, which means the tubular DMFC loses more fuel than the planar DMFC. The total run time of each constant voltage test also increased as the methanol concentration increased, due to more fuel available for the fuel cell to operate a longer period of time.

Considering the higher static fluid pressure in the tubular fuel cell than the planar fuel cell based on the orientation and structure of both cells, it is clear that as the run time increased that more methanol was lost due to crossover in the tubular fuel cell. This shows that the methanol crossover is also dependent upon time in the tubular fuel cell since both the fuel and energy efficiencies decreased as the methanol concentration, and associated run time, increased. Unlike the tubular DMFC, the planar DMFC was much more resistant to methanol crossover and maintained

higher fuel and energy efficiencies even as the methanol concentration and run time both increased. In other words, the methanol crossover is higher in the tubular DMFC than in the planar DMFC due to a higher static fluid pressure in the tubular AFR. Future efforts are needed to reduce the methanol crossover in the tubular fuel cell by increasing the mass transport resistance at the anode with the addition of another, lower porosity, gas diffusion layer.

4. Conclusions

A novel tubular-shaped, passive DMFC that operates with methanol solution in a central AFR and oxygen provided by the air was investigated. A tubular frame was designed and fabricated based on the existing planar, passive DMFC frame to provide fuel channels, current collectors, compression across the MEA, and to hold the MEA in a tubular shape. Nafion® 212 and 115 CCMs were used to produce MEAs with the addition of GDLs to either side of the CCMs. Also, a planar, passive DMFC was built and tested with identical MEAs for comparison. The following conclusions were made:

1. The performance of the Nafion® 115 MEA was better than that of the Nafion® 212 MEA due to decreased methanol crossover and reduced de-lamination of the MEA (attributed to methanol crossover).
2. The tubular DMFC produced $19.4\,\mathrm{mW\,cm^{-2}}$ with the 2 M methanol solution, which represents an 870% improvement in power from the previous best, passive, tubular DMFC.
3. The peak power density of the tubular DMFC was higher than that of the planar DMFC for both the Nafion® 212 and 115 MEAs operated with 1 M, 2 M, and 3 M methanol solutions.
4. The tubular DMFC produced equal fuel and energy efficiencies to those of the planar DMFC during 1 M methanol operation and with the Nafion® 212 MEA, but the fuel and energy efficiencies of the tubular DMFC were higher than those of the planar DMFC during the 1 M methanol operation and with the Nafion® 115 MEA.
5. The planar DMFC produced higher fuel and energy efficiencies than those of the tubular DMFC for both Nafion® 212 and 115 MEAs with 2 M and 3 M methanol solutions due to increased methanol crossover in the tubular fuel cell.
6. The tubular DMFC experienced higher methanol crossover than the planar DMFC potentially due to an increased static fluid pressure in the AFR caused by cell orientation and geometry.

Acknowledgement

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