Micro-Tubular Flame-assisted Fuel Cells Running Methane

Ryan J. Milcarek^{a,*}, Michael J. Garrett^a, Kang Wang^a, Jeongmin Ahn^a

^aDepartment of Mechanical and Aerospace Engineering,
Syracuse University, Syracuse, NY 13244 USA

Abstract:

Direct flame fuel cells (DFFCs) have been investigated as an alternative means of combustion based power generation devices, but current challenges for this technology have included low fuel utilization and efficiency. In order to overcome these obstacles a new micro-tubular flame-assisted fuel cell (mT-FFC) concept is developed in this work and its performance is assessed at different equivalence ratios and temperatures. The concept is based on fuel-rich combustion exhaust, with the combustion equivalence ratio controlled and the exhaust flowing through the fuel cell for complete electrochemical energy conversion. The results were compared to a hydrogen baseline with the same electron potential as the fuel-rich exhaust. The mT-FFC concept offers significant advantages including high fuel utilization and greater performance stability compared to DFFCs.

Keywords: Flame-assisted fuel cell; Micro-tubular solid oxide fuel cell; Solid oxide fuel cell (SOFC); Combined heat and power (CHP); Fuel-rich combustion

* Corresponding author. Tel.: 315 443 9309; Fax: +1 315 443 9099.

E-mail address: rjmilcar@syr.edu (R. Milcarek).

1. Introduction

Direct flame fuel cells (DFFCs) are novel energy conversion devices that consist of a solid oxide fuel cell (SOFC) in direct contact with a flame to generate power [1,2]. The flame acts as a partial oxidation reformer that can operate on a wide variety of solid, liquid and gaseous fuels while simultaneously providing heat for the SOFC operation [1-14]. Within the flame, H₂ and CO (syngas) and unburned hydrocarbons are available for electrochemical conversion in the SOFC. Due to the simplicity of the setup, DFFCs have advantages over the more traditional dual chamber SOFC [15-17] and single chamber SOFC [18-21] including high fuel flexibility, rapid start-up and shut-down, and no complex thermal management, chamber or sealant required. In terms of fuel cell systems, the use of combustion is advantageous because it combines the thermal management and fuel processing systems into one. These advantages could allow DFFCs to be integrated with traditional combustion technologies such as boilers or furnaces for Combined Heat and Power (CHP) generation. While recent advances in DFFC power density are promising [3,4], the overall electrical efficiency of these systems remains low due to low fuel utilization (<1%) and low electrical efficiency [3,4,7], making the heat-to-power ratio impractical for traditional CHP systems. Improvements in SOFC design and fabrication can help improve the fuel utilization, but Wang *et al.* noted that the difference in gas combustion kinetics compared to electrochemical kinetics makes high fuel utilization difficult to achieve [7]. Obtaining higher fuel utilization has been considered as a primary obstacle for DFFCs and has not been fully resolved at this time.

Among the many different fuel cell geometries used for SOFCs, micro-tubular SOFCs (mT-SOFCs) have received considerable attention due to several advantages including thermal shock resistance, good mechanical strength, rapid start-up and shut-down. Many of the advantages inherent in the mT-SOFC geometry make them ideal candidates for use in a DFFC setup. In addition, the mT-SOFC geometry allows the flame and exhaust to be effectively separated from the cathode side and thus can

1 improve the oxygen partial pressure gradient across the cell and the open circuit voltage (OCV).
2 Unfortunately, the internal diameter of a mT-SOFC, which is a few millimeters or less by definition [22-
3 33], is below the quenching distance of traditional hydrocarbon fuels, such as methane, ethane, propane
4 and methanol, which prevents flame propagation [34,35]. While it is not possible to operate the mT-
5 SOFC with a direct flame on the tube interior, which is needed for a DFFC setup, the mT-SOFC could
6 operate in fuel-rich combustion exhaust. A distinction is made here between the **original** DFFC and the
7 flame-assisted fuel cell (FFC). **Figure 1A** illustrates the traditional DFFC, which has a burner with pre-
8 mixed fuel and air that is open to the ambient. With the burner open to the ambient, excess air ensures
9 complete combustion and the setup should more accurately be considered a partially premixed flame. In
10 many DFFC studies, the equivalence ratio is defined for the premixed conditions, but because the flame
11 is open to the ambient little to no fuel exists in the exhaust. As a result, the DFFC setup typically has the
12 SOFC operate directly in the flame where some unburned fuel or syngas is available for electrochemical
13 energy conversion. **Figure 1B** illustrates the flame-assisted fuel cell concept where the flame is partially
14 enclosed which controls the final combustion equivalence ratio. Thus, the FFC can be considered a
15 perfectly premixed combustion system because no other excess air mixes with the premixed fuel/air
16 mixture. With no excess air, the combustion equivalence ratio is controlled and the SOFC can operate in
17 the combustion exhaust where excess fuel (i.e. syngas or hydrocarbons) exists. The SOFC still operates
18 near the flame so that the combustion acts as both a fuel reformer and a heat source. Although the DFFC
19 and FFC are similar, the exhaust composition is very different because excess air is not present for
20 complete combustion in the FFC. While the equivalence ratio of the combustion is also defined at a
21 similar location for both setups, the final or overall equivalence ratio for a DFFC would need to take into
22 account the excess air which often means that the equivalence ratio is below stoichiometry.

Fig. 1. Schematic of the A) direct flame fuel cell (DFFC) setup compared to the B) flame-assisted fuel cell (FFC) setup discussed in this work.

With the FFC defined, operation of a mT-SOFC in the combustion exhaust gives rise to the micro-tubular flame-assisted fuel cell (mT-FFC). **Figure 2** shows a schematic of a mT-FFC setup. In this setup, the fuel and air can be premixed or non-premixed as long as there is excess fuel **overall** and fuel-rich combustion results. The fuel-rich exhaust is then fed through a mT-SOFC where the remaining fuel is electrochemically converted to water and carbon dioxide. This concept was proposed recently operating in a furnace exhaust [36]. To gain a comprehensive understanding of the potential of this energy conversion concept, the fuel cells performance at different equivalence ratios and temperatures needs to be assessed. Herein we report a mT-FFC operating in methane combustion exhaust. The SOFCs performance was assessed over a range of equivalence ratios and temperatures to assess the potential of this combustion based power generation device. The performance in combustion exhaust was compared to the performance in hydrogen, which is the ideal fuel for fuel cells.

Fig. 2. micro-Tubular Flame-assisted Fuel Cell (mT-FFC) setup.

2. Experimental Setup

2.1 Combustion Characterization

Figure 3 is a schematic of the combustion characterization apparatus. Methane was chosen as the fuel for this study because it is the primary constituent of natural gas, which is a typical fuel for boilers and furnaces. The combustion chamber inshot burner used in this study is the same size as inshot burners from residential size furnaces. In order to achieve conditions comparable to a typical residential furnace, the heat of combustion for natural gas was matched to a 29.3 kW (100,000 BTU.hr⁻¹) residential furnace operating at stoichiometry, which allowed the methane flowrate to be determined (~10 L.min⁻¹ for each inshot burner, typically 5 inshot burners for a residential furnace). The flow rate of methane was then fixed during combustion characterization and the air flow rate varied in order to obtain the desired equivalence ratio. The equivalence ratio, Φ , is defined in Eq. (1),

$$\Phi = \frac{n_{fuel}/n_{air}}{n_{fuel}^s/n_{air}^s} \quad (1)$$

where n_{fuel} and n_{air} are the molar flow rates of fuel and air respectively, and n_{fuel}^s and n_{air}^s are the molar flow rates of fuel and air for stoichiometric combustion. The flow rate of the air and methane was regulated with LabView software and mass flow controllers. The combustion exhaust was removed from the combustion chamber with a syringe and then directed into a gas chromatograph (GC) for analysis. Thermocouples were placed along the length of the combustion chamber to measure the temperature of

1 the flame and exhaust. A thorough description of the combustion chamber testing was already reported
 2 elsewhere [37].

3
 4 **Fig. 3.** Combustion characterization apparatus.

5 **2.2 Fuel Cell Fabrication and Characterization**

6 An anode supported mT-SOFC (AS-SOFC) was prepared by extrusion of the anode and wet-
 7 powder spraying of the electrolyte and cathode. Yttria-stabilized zirconia (YSZ, Tosoh), nickel oxide
 8 (NiO) + YSZ (60:40 w/w, J.T.Baker) and lanthanum strontium manganite (LSM, $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{MnO}_{3-x}$)
 9 + YSZ (Fuel Cell Materials, 50:50 w/w) were used as the electrolyte, anode, and cathode materials,
 10 respectively. The anode was extruded and then sintered at 1000°C for 4h. The sintered anode has an
 11 internal diameter of 2.4mm and an outer diameter of 3.2mm. The YSZ was then spray deposited onto the
 12 anode surface using a spraying gun and then fired at 1400°C in air for 4h. The sintered electrolyte was
 13 6μm thick. LSM + YSZ was deposited similarly and then sintered at 1100°C for 2h to form the complete
 14 fuel cells with a cathode layer. The active area based on the inside diameter is 1.67cm².

15 The I-V (current–voltage) method with the 4-probe technique was used to investigate the
 16 electrochemical behavior of the mT-FFC. The open circuit voltage (OCV), power density and
 17 polarization were assessed using a Keithley 2420 sourcemeter interfaced with a computer for data

acquisition. A K-type thermocouple was attached to the cathode surface to measure the instantaneous temperature of the fuel cell.

2.3 Testing Setup

The mT-SOFCs were first tested with hydrogen fuel at flow rates of 9.3 mL.min⁻¹, 12.9 mL.min⁻¹, 22.1 mL.min⁻¹, 28.5 mL.min⁻¹, 33.5 mL.min⁻¹, 43.7 mL.min⁻¹, 45.8 mL.min⁻¹. The hydrogen flow rates were selected to match the electron potential of the methane exhaust, as described in the results section. Following the testing with hydrogen, the fuel cell was tested with a model fuel that simulates methane exhaust composition at equivalence ratios of 1.1, 1.15, 1.2, 1.25, 1.3, 1.35, and 1.4. For each equivalence ratio, the primary composition of the dry exhaust was found to be H₂, CO, CO₂ and N₂. Therefore, only these gases were used for the model fuel-rich exhaust. **Table 1** shows the flow rates of H₂, CO, CO₂ and N₂ into the 1.67cm² mT-FFC for each equivalence ratio. As an example of how the flow rates in **Table 1** were determined, the model fuel flow rate at an equivalence ratio of 1.4 will be explained here. The total fuel and oxidant flow rate into the 29.3 kW furnace at an equivalence ratio of 1.4 is 390 L.min⁻¹ (methane flow rate of 10 L.min⁻¹ per inshot burner and air flow rate of 68 L.min⁻¹ per inshot burner times 5 inshot burners). The total flow of fuel and oxidant into the furnace must pass through a 4 fuel cell stack design having a total active area of 3,000cm². The flowrate per cm² can be calculated by taking the total flow rate into the furnace (390 L.min⁻¹) and dividing by the total fuel cell area of 3,000cm². This calculation yields 130 mL.min⁻¹.cm⁻² at an equivalence ratio of 1.4. Because the flow rate of methane was fixed and the air flow rate varies, the total flow rate per unit surface area varies with equivalence ratio. However, the fuel flow rate per cm² into the furnace is fixed at 16.7 mL.min⁻¹.cm⁻² (based on 10 L.min⁻¹ per inshot burner times 5 inshot burners divided by the total fuel cell stack area) for all equivalence ratios because the fuel flow rate was fixed. For the 1.67cm² mT-SOFC used in this study, the total flowrate is 217 mL.min⁻¹ at an equivalence ratio of 1.4. The exhaust composition was measured during the combustion characterization with a GC and therefore does not include water. The model fuel

based on this dry exhaust measured with the GC was found to be consistent within $\pm 5\%$. The volume percent of each exhaust component measured by the GC was multiplied by the total flow rate into the fuel cell (217 mL.min^{-1} for the case of 1.4) in order to determine the flow rates of each exhaust component shown in **Table 1**. **Table 1** is based completely on the GC analysis and not upon an analytical solution. The GC analysis results are shown in the Results and Discussion section. A mass flow controller interfaced with LabView software was used to regulate the H_2 , CO , CO_2 and N_2 in each case.

Table 1: Flow rates of the model fuel-rich exhaust species into the 1.67 cm^2 mT-FFC at different equivalence ratios based on a fixed flow rate of methane into the furnace of $16.7 \text{ mL.min}^{-1}.\text{cm}^{-2}$.

Equivalence ratio	H_2 (mL.min^{-1})	CO (mL.min^{-1})	CO_2 (mL.min^{-1})	N_2 (mL.min^{-1})	Total (mL.min^{-1})
1.10	2.9	6.5	30.4	228.4	268
1.15	4.6	8.3	27.4	217.5	258
1.20	10.7	11.5	24.8	201.3	248
1.25	15.3	13.3	22.0	188.6	239
1.30	18.5	15.0	19.7	177.7	231
1.35	25.8	18.0	18.5	161.4	224
1.40	27.0	18.9	16.4	154.3	217

3.0 Calculation

In order to assess the experimental results, the reversible cell potential must be calculated based on the model fuel-rich combustion exhaust composition given in **Table 1**. Combustion exhaust varies based on the fuel, equivalence ratio, temperature, pressure and burner characteristics (e.g., complete mixing). In general, partial oxidation or fuel-rich combustion generates syngas along with the traditional products of combustion. For stoichiometric combustion, the reaction can be written as Eq. (2) where $\gamma = x + y/4 - z/2$. For partial oxidation the reaction can be written similarly as Eq. (3), but with additional combustion products, which are primarily H_2 and CO for many fuels over a range of equivalence ratios. In Eq. (3), $x = B + C$, $y = 2(A + D)$, and $z + 2\gamma = B + 2C + D$.

For methane (CH₄), Eq. (3) can be written as Eq. (4).

Clearly with only 3 equations and 4 unknowns (i.e., A, B, C and D), the equation is not solvable analytically. Additional relations for chemical equilibrium analysis or experimental results are necessary. Assuming chemical equilibrium A, B, C, and D can be determined using one of many different chemical equilibrium software programs available. Experimental determination typically occurs through a mass spectrometer or a gas chromatograph. After determination of the exhaust composition, the theoretical fuel cell voltage can be determined using the general Eq. (5).

$$E_{rev} = \frac{-\Delta g}{nF} \quad (5)$$

Here n is the number of electrons per mole of fuel (e.g. n is 2 for both H₂ and CO), F is Faradays constant (i.e. 96,485 C.mol⁻¹) and Δg is the change of Gibbs free energy for the fuel cell electrochemical reaction. In this case, the reaction is Eq. (6). Note that a, b, c, d and e are mole fractions of the model combustion exhaust species and thus a + b + c + d + e ≈ 1 because all other combustion exhaust species are relatively trace.

It can easily be shown that, $g = b + c$ and $h = a + d$. Thus, the following equation results (7).

To determine Δg, for the fuel cell voltage calculation (Eq. 5), only a portion of the information contained in Eq. (7) is necessary. For instance, the c moles of CO₂, d moles of H₂O and all the moles of N₂ do not participate in the electrochemical reaction and their contributions to the change in Gibbs energy would cancel assuming an isothermal reaction. Thus, Δg only requires the following equation (8).

It can then be shown that $b + 2f = 2b + a$ or $f = (a + b)/2$. Thus the change in Gibbs free energy between b moles of CO_2 and a moles of H_2O minus a moles of H_2 , b moles of CO and e moles of O_2 will give the required Δg . The variable n depends on the fuel. For 1 mole of H_2 there are 2 moles of electrons. The same is true for CO . As a result, if there is 1 mole of syngas, then there are 2 moles of electrons. In this case, there is less than one mole of fuel based on a and b being the mole fractions of each species in the exhaust composition. This can be accounted for in one of two ways. First, 1 mole of combustion exhaust ‘fuel’ also includes CO_2 , N_2 and H_2O . Therefore, $n = 2(a + b)$ moles of electrons per mole of our fuel leading to Eq. (9).

$$E = \frac{-\Delta g}{2(a+b)F} \quad (9)$$

Alternatively, for one mole of syngas, $a + b$ must equal 1. Therefore, Eq. (8) can be rewritten for one mole of syngas with the same ratio of H_2 to CO as in Eq. (7) as to give Eq. (10).

Mathematically, this is equivalent to determining the change in Gibbs free energy according to (8) and then dividing by $a + b$. This turns out to be the same as equation (9) so long as Δg is for reaction (8) not reaction (10). The specific Gibbs free energy for each species at different temperatures can be obtained from thermodynamic tables. Obtaining the coefficients (i.e. a , b , c , d , and e) from the experimental data reported previously [36,37] the following table can be constructed.

Table 2: Mole fractions for methane/air combustion under atmospheric conditions and the fuel-air equivalence ratio varying from 1.05 to 1.4.

Species	Coeff.	Equivalence ratio							
		1.05	1.1	1.15	1.2	1.25	1.3	1.35	1.4
H ₂	a	0.0001	0.0107	0.0179	0.0430	0.0638	0.0801	0.1153	0.1243
CO	b	0.0141	0.0242	0.0323	0.0461	0.0557	0.0648	0.0803	0.0873
CO ₂	c	0.1157	0.1132	0.1064	0.0997	0.0920	0.0853	0.0827	0.0758
N ₂	e	0.8703	0.8519	0.8435	0.8112	0.7885	0.7697	0.7217	0.7126
O ₂	f	0.0071	0.0174	0.0251	0.0445	0.0598	0.0725	0.0978	0.1058
	a + b	0.0142	0.0349	0.0501	0.0891	0.1195	0.1450	0.1955	0.2117

The fuel cell voltage based on the syngas composition can then be calculated based on Eqs. (8) and (9). While the voltage calculated according to Eq. (9) is correct based on the syngas composition, temperature, and pressure only, the dilution of the fuel must also be taken into account. This is done by using the Nernst equation Eq. (11).

$$E_{rev} = E_{syngas} - \frac{RT}{nF} \ln (K) \quad (11)$$

Here K is the equilibrium constant which can be calculated using Eq. (12).

$$K = \prod_{i=1}^N \left(\frac{P_i}{P} \right)^{(\vartheta_i'' - \vartheta_i') / \vartheta_F'} \quad (12)$$

Assuming ideal gas behavior, the partial pressure ratio (P_i/P) is equal to the mole fraction. In this case, ϑ_F' is 1 as there is 1 mole of syngas according to (10). Eq. (13) for K can then be written and calculated assuming the air is 21% O₂ and the only fuels reacting are H₂ and CO. Note that the mole fractions (X_i) of fuel are obtained from Eq. (7) while the coefficients $(\vartheta_i'' - \vartheta_i') / \vartheta_F'$ are obtained from the electrochemical reaction Eq. (10).

$$K = X_{O_2}^{-f/(a+b)} \cdot X_{H_2}^{-a/(a+b)} \cdot X_{CO}^{-b/(a+b)} \quad (13)$$

Thus, the following theoretical fuel cell voltage can be calculated for the fuel cell exhaust composition for the experimentally obtained exhaust composition.

Table 3: Theoretical fuel cell voltage for the dry combustion exhaust composition

at different temperatures (700-800°C) and combustion equivalence ratios at atmospheric pressure.

Temp. (°C)	1.05	1.1	1.15	Equivalence ratio				
	1.2	1.25	1.3	1.35	1.4			
700	0.936	0.930	0.940	0.954	0.963	0.970	0.980	0.984
720	0.923	0.918	0.928	0.943	0.953	0.960	0.971	0.974
740	0.909	0.905	0.917	0.933	0.942	0.950	0.961	0.965
760	0.896	0.893	0.905	0.922	0.932	0.940	0.951	0.955
780	0.882	0.881	0.894	0.911	0.922	0.930	0.942	0.945
790	0.876	0.875	0.888	0.906	0.917	0.925	0.937	0.941
800	0.869	0.869	0.882	0.900	0.911	0.920	0.932	0.936

4.0 Theory

With the reversible cell potential derived, determination of the efficiency of the mT-FFC proceeds in a similar fashion to the DFFC as described elsewhere [7], but with slight variations because the exact amount of syngas in the exhaust is known. With the model combustion exhaust composition established, the efficiency is the product of the fuel utilization $\varepsilon_{F.U.}$, and the SOFC electrical efficiency ε_{el} . The fuel utilization efficiency accounts for the amount of syngas actually utilized in the electrochemical reactions compared to the amount available. Thus the fuel utilization efficiency can be defined by Eq. (14).

$$\varepsilon_{F.U.} = \frac{H_2 \text{ and CO consumed in SOFC}}{\text{Total } H_2 \text{ and CO available in exhaust}} \quad (14)$$

Calculation of the fuel utilization proceeds according to Eq. (15).

$$\varepsilon_{F.U.} = \frac{i}{\frac{V_{fuel}}{V^M} \frac{1000}{60} nF} \quad (15)$$

In Eq. (15), i [A] is the current being drawn from the SOFC, V_{fuel} [mL.min⁻¹] is the total flow rate of syngas (i.e., the sum of the flow rate of H₂ and CO from **Table 1**), V^M [m³.mol⁻¹] is the molar volume at standard conditions, which is 2.24×10^{-2} m³.mol⁻¹, n is the moles of electrons per moles of

fuel (i.e., 2 for syngas as $n=2$ for both H_2 and CO) and F is Faradays constant. The numerical constants in Eq. (15) are for unit conversion.

The electrical efficiency of the SOFC has been defined in different, but equivalent ways in the literature. The definition based on the operating voltage (V) and the thermo-neutral voltage (V_{th}) is used here as defined by Eq. (16) with the thermo-neutral voltage defined by (17).

$$\varepsilon_{el} = \frac{V}{V_{th}} \quad (16)$$

$$V_{th} = \frac{-\Delta h}{nF} \quad (17)$$

The enthalpy of reaction, Δh , is calculated based on Eq. (8).

5.0 Results and Discussion

Figure 4 shows the results of the combustion characterization. The rich flammability limit of methane was at an equivalence ratio of 1.4. Although this result is lower than published values for methane, the flammability limits are ultimately found to be apparatus dependent [35]. The fuel-lean ($\Phi < 1$) conditions were not investigated fully because the mT-FFC concept relies upon fuel-rich exhaust. As expected, the concentration of O_2 decreased until it was ~ 0.1 Vol% or less at equivalence ratios of 1.1 and above. Due to the small contribution of O_2 to the exhaust composition, it was neglected in the model fuel for the mT-FFC testing. After passing stoichiometry ($\Phi > 1$) the concentration of H_2 and CO grew as expected. Both H_2 and CO can be used directly in electrochemical conversion for power generation. They represent the primary fuel for mT-FFC operation. However, their concentrations are significantly diluted by the presence of high concentrations of N_2 and CO_2 . One of the important results is that CH_4 was not detected in the exhaust at any of the equivalence ratios tested, which indicates good mixing and combustion of the fuel. In addition, CH_4 is known to cause carbon coking of Ni based anode materials used for SOFCs, which is detrimental to long term performance. With appropriate mixing and combustion, much of the CH_4 can be eliminated in the fuel-rich exhaust, which can help prevent carbon

1 coking of the anode. Thus, mT-FFCs have potential for improved coking tolerance when CH₄ is
 2 eliminated from the exhaust.

Fig. 4. Methane combustion characterization results showing temperature and exhaust composition variations with equivalence ratio.

6 The combustion characterization also indicated relevant temperatures for SOFC operation.
 7 Traditional fuel cell materials used for SOFC's require operating temperatures of 800-1000°C. Despite
 8 having an uninsulated combustion chamber, the exhaust temperatures remained above 800°C at an
 9 equivalence ratio of 1.4, even at 10 cm downstream of the flame. As a result, traditional fuel cell
 10 materials can be used for the mT-FFC operation. In addition, doped-ceria materials, which are employed
 11 for many DFFC studies, can also be used at locations further downstream. Overall, the combustion
 12 characterization results indicate that the temperatures are relevant for mT-FFCs to be placed in the
 13 exhaust of a traditional, residential size furnace for CHP applications. **A mT-SOFC was held in the**
 14 **combustion exhaust and the temperature on the tube interior was monitored with a thermocouple. Table**
 15 **4 shows the results. The anode temperature follows a similar trend as the combustion temperature in Fig.**
 16 **4, but with much smaller changes in temperature overall. The results further indicate that a mT-FFC can**

operate in combustion exhaust around 800°C or lower depending on the placement of mT-FFC relative to the flame.

Table 4: Anode temperature as the combustion equivalence ratio is varied.

Equivalence ratio	Anode temperature (°C)
1.1	829
1.2	826
1.3	825
1.4	805

In order to assess the mT-FFCs performance while operating on fuel-rich methane combustion exhaust, a baseline is needed. Hydrogen is the ideal fuel for fuel cell operation. However, because hydrogen is not readily available, the use of other hydrocarbons is advantageous for all types of fuel cells. Therefore, the fuel-rich exhaust is compared in this study with hydrogen fuel. In order to have an equivalent potential for power generation, the number of electrons available for electrochemical reactions was matched between the fuel-rich exhaust and hydrogen. For example, using pure H₂ results in 2 moles of electrons for each mole of H₂ electrochemically oxidized. As shown above, fuel-rich exhaust was found to consist primarily of H₂, CO, CO₂ and N₂. The N₂ and CO₂ do not participate directly in the reaction leaving only CO and H₂, or syngas. Electrochemical oxidation of CO results in 2 moles of electrons for each mole of CO. However, much higher flowrates of exhaust composition are needed to match the electron potential of pure hydrogen with that of the exhaust stream. As a result, the flowrates of hydrogen and the fuel-rich exhaust vary significantly. For example, to match the exhaust composition at an equivalence ratio of 1.1 and flowrate of 268.2 mL.min⁻¹, the hydrogen flow rate needed was only 9.3 mL.min⁻¹. Due to the increase in syngas concentration with equivalence ratio, the flowrate of H₂ needed to create the baseline increases with increased equivalence ratio, despite a decrease in the exhaust flowrate. The H₂ baselines are shown in **Fig. 5**. The mT-SOFC achieve peak

1 power densities at 800°C of 149, 217, 414, 504, 542, 583 and 586 mW.cm⁻² at H₂ flowrates of 9.3, 12.9,
 2 22.1, 28.5, 33.5, 43.7 and 45.8 mL.min⁻¹, respectively.

3 **Fig. 5.** mT-SOFC performance at 800°C with hydrogen flowrate from 9.3 to 45.8 mL.min⁻¹.
 4

5 With the baseline established, the performance of the mT-FFC was assessed while operating with
 6 the model fuel-rich exhaust composition. The flowrates of H₂, CO, CO₂ and N₂ at each equivalence ratio
 7 were shown in Table 1 and will not be repeated here. As shown in **Fig. 6** the mT-FFC achieved
 8 significant power at all equivalence ratios between 1.1 and 1.4. The peak performances of the mT-FFC
 9 at 800°C was 71.3, 94.8, 116.9, 144.8, 169.1, 216.1, and 234.9 mW.cm⁻² at equivalence ratios of 1.1,
 10 1.15, 1.2, 1.25, 1.3, 1.35 and 1.4, respectively. The OCV of the mT-FFC decreased from the H₂ baseline
 11 from 1.03 to 0.92 V at an equivalence ratio of 1.4, which was in close agreement with the reversible cell
 12 potential calculations given in section 3. This reduction is a direct result of Nernstian losses which are
 13 related to the increased concentration of inert and other non-reacting gases in the fuel stream. This trend
 14 continues at lower equivalence ratios, with an OCV of 0.69 V at an equivalence ratio of 1.1 compared to
 15 0.9 V for the H₂ baseline of 1.1. At lower equivalence ratios, the concentration of syngas in the exhaust
 16 is reduced. This results in a decreasing OCV with decreasing equivalence ratio. The decrease in the

1 OCV of the H_2 baseline is also a result of decreased concentration of fuel at the triple phase boundary,
 2 but it is caused by the presence of O_2 diffusing from the outlet of the mT-FFC when the flowrate is low.
 3 This can be verified because the OCV of the H_2 baseline curves in **Fig. 5** remains at or above 1.0 V until
 4 the flowrate is at or below 12.9 mL.min^{-1} whereas the OCV decreases steadily with decreasing
 5 equivalence ratio in the case of the fuel-rich exhaust shown in **Fig. 6**.

Fig. 6. mT-FFC operating at 800°C with a model fuel-rich exhaust composition between equivalence ratios of 1.1 and 1.4.

One of the differences of the FFC performance compared to DFFCs is the relative stability of the power and polarization curves. As shown in **Fig. 6** the power curve is relatively stable throughout the test while the power curve of a DFFC tends to oscillate during testing [3,4] as a result of fluctuations in the flame while open to the ambient. This fluctuation can present problems in controlling and maintaining a stable operating condition for DFFCs. However, the most significant result of the mT-FFC testing is the high fuel utilization achieved. The definition of fuel utilization was given by Eq. (14) [7].

At peak power density, the mT-FFC achieved a fuel utilization of 10.6% while operating at an equivalence ratio of 1.4. Although this result is less than complete fuel utilization, it is still 2 orders of

1 magnitude higher than the fuel utilization achieved by DFFCs. This marks a breakthrough in fuel
2 utilization of FFCs, which makes the electrical efficiency of these devices much more promising for
3 implementation. In addition, the mT-SOFC only achieved a fuel utilization of 32.4% at peak power
4 density with pure hydrogen. From this result it is evident that the mT-FFC could likely achieve a much
5 higher fuel utilization if the microstructure of the fuel cell material was improved and the mT-SOFC
6 achieved 90% or greater fuel utilization with hydrogen. In addition, it is well known that decreasing the
7 fuel flow rate in the fuel-rich exhaust could also achieve similar results. For example, as the equivalence
8 ratio decreases from 1.4 to 1.2, the fuel utilization increases from 10.6% to 15.1%. The increase in fuel
9 utilization at lower equivalence ratios results from a decrease in the syngas flowrate (from 45.9 to 22.2
10 mL.min⁻¹) with decreasing equivalence ratio. An increase in fuel utilization with a decrease in hydrogen
11 flowrate is also observed for the mT-SOFC results.

12 **Figure 7** shows the mT-FFC's performance and polarization curves at an operating temperature
13 of 700°C. The mT-FFC still achieved high performance at higher equivalence ratios with peak power
14 densities of 43.3, 44.8, 73.5, 98.8, 118.7, 147.5 and 155.2 mW.cm⁻² at equivalence ratios of 1.1, 1.15,
15 1.2, 1.25, 1.3, 1.35, and 1.4, respectively. Despite the operating temperature, which is low for the LSM
16 ((La_{0.8}Sr_{0.2})_{0.95}MnO_{3-x}) based cathode used in this study, the performance was significant and the fuel
17 utilization was not altered significantly. Better performance is expected if a cathode with higher catalytic
18 activity is used at these lower temperatures. Based on these results, a CHP system with mT-FFCs could
19 extract some of the heat for space heating prior to having the fuel-rich exhaust enter the fuel cells. This
20 allows for the electrical and heating efficiencies to be adjusted based on the placement of the mT- FFCs
21 relative to the furnace inshot burner.

Fig. 7. mT-FFC operating at 700°C with a model fuel-rich exhaust composition between equivalence ratios of 1.1 and 1.4.

Figure 8 is a comparison of the mT-FFC's with the mT-SOFC's having the same electron potential, as described previously. For example, H_2 at a flowrate of 45.8 mL.min^{-1} has the same number of electrons available for electrochemical conversion per unit time as the fuel-rich exhaust at an equivalence ratio of 1.4. The fuel-rich exhaust achieved 28.2%, 31.2 % and 40.1% of the H_2 baseline at equivalence ratios of 1.2, 1.3 and 1.4, respectively. There is a trend towards increased performance relative to the H_2 baseline with increasing equivalence ratio. This result can be attributed to higher fuel concentration at higher equivalence ratios. This is not a result of increased fuel utilization, as the fuel utilization decreases with increasing equivalence ratio, as described previously.

Fig. 8. Comparison of the mT-FFC performance operating at 800°C in the model fuel-rich exhaust at equivalence ratios of 1.2, 1.3, 1.4 with the hydrogen baseline at equivalent electron potentials.

As the fuel utilization is a key challenge for DFFCs and the mT-FFC has potential for much higher fuel utilization, the fuel utilization and electrical efficiency were investigated as the equivalence ratio, fuel cell operating voltage and flow rates were adjusted. The results are given in **Fig. 9**. Calculation of the fuel utilization and electrical efficiency was conducted according to the equations given in section 4. The flow rates were varied by scaling the **Table 1** flow rates to 60%, 70%, 80%, 90%, 100%, 110%, 120% and 130% of the full value. For example, 100% of the **Table 1** values represents the **Table 1** values themselves while 60% would represent a 60% reduction in flow rate for each exhaust species. **Figure 9** clearly shows that the fuel utilization and electrical efficiency of the mT-FFC vary with the equivalence ratio under the test conditions. When more fuel is available (i.e., syngas) at higher equivalence ratios, the flow rates needed to optimize efficiency are much lower as the mT-FFC cannot utilize all of the fuel available. A peak fuel utilization of 34.2% and electrical efficiency of 12.4% was achieved for the conditions studied at an equivalence ratio of 1.2, flow rates that are 60% of the **Table 1**

values and a mT-FFC operating voltage of 0.5 V. Full optimization of the electrical efficiency will depend on the specific mT-SOFC micro structure, but the fuel utilization and electrical efficiency can certainly be improved by varying the conditions described here. Even without optimization, the electrical efficiency is significantly higher than the optimized efficiency ($\sim 0.19\%$) of a DFFC operating with methane fuel.

Fig. 9. Fuel utilization and electrical efficiency with exhaust flow rates from 60% up to 130% of the Table 1 values, fuel-rich exhaust equivalence ratios from 1.2 - 1.4 and mT-FFC operating voltages of a) 0.7 V and b) 0.5 V.

As described previously, the polarization and power curves are notably smoother than the typical DFFC results. To compare the performance stability of the mT-FFC to the DFFC, a short term test was conducted on the mT-FFC at a constant current density of 133 mA.cm^{-2} for 5 h. The results are compared to those obtained for a planar DFFC operating with methane [3], which had similar power density at a constant current density loading of 200 mA.cm^{-2} . Figure 10 provides the comparison over the 5 h period with data obtained every 10 min. The DFFC had a maximum change in power density of 7.2 mW.cm^{-2} between readings while the mT-FFC had a maximum fluctuation of 0.25 mW.cm^{-2} . The smaller fluctuation in power density between readings demonstrates the improved performance stability that result from operating in exhaust instead of operating directly in a flame open to the ambient. The

DFFC performance fluctuation was attributed to atmospheric variation which causes the flame and power density to oscillate slightly [3]. After the initial 5 h test, the current density loading was increased to 200 mA.cm^{-2} to be at the same loading as the previous study and the short term test was continued for another 20 h. The power density remained extremely stable over the total 25 h test.

Fig. 10. Short term test and comparison of the mT-FFC performance with a current density loading of 133 mA.cm^{-2} with a DFFC operating with methane fuel from [3].

Carbon deposition on Ni based anodes is a well-known problem that proceeds according to several reactions. Direct use of methane can result in carbon deposition according to Eq. (18) while the use of CO can lead to carbon deposition through the inverse Boudouard reaction Eq. (19) or by reacting with H_2 through Eq. (20) [38,39]. Each of these reactions presents a potential challenge for both DFFC and the mT-FFC concept. However, stable performance of the mT-FFC after 25 h is promising. In addition to carbon deposition through the mechanisms described, the DFFC has also been shown to have soot formation on the anode surface. No soot formation was observed on the anode of the mT-FFC after the 25 h testing, demonstrating an additional advantage of not operating directly in the flame.

6. Conclusions

Despite having highly diluted syngas from fuel-rich combustion exhaust, mT-FFCs were able to generate more than 40% of the peak power of a mT-SOFC operating on pure hydrogen. In addition, the mT-FFC operating in fuel-rich combustion exhaust at an equivalence ratio of 1.4 was able to achieve 32.7% of the fuel utilization at peak power density obtained with pure hydrogen having the same electron potential. The mT-FFC offers advantages over the traditional DFFC including increased fuel utilization and improved performance stability. In addition, the fuel-rich exhaust can be more easily separated from the cathode which can improve the oxygen partial pressure gradient across the cell and the OCV. More work is needed to fully investigate the potential for fuel flexibility, rapid startup and shutdown, but mT-FFCs have potential to maintain these advantages compared to single chamber and dual chamber SOFCs. The significant advances in fuel utilization and performance stability make mT-FFCs candidates for combustion based micro-CHP systems.

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FIGURE CAPTIONS

Fig. 1. Schematic of the A) direct flame fuel cell (DFFC) setup compared to the B) flame-assisted fuel cell (FFC) setup discussed in this work.

Fig. 2. micro-Tubular Flame-assisted Fuel Cell (mT-FFC) setup.

Fig. 3. Combustion characterization apparatus.

Fig. 4. Methane combustion characterization results showing temperature and exhaust composition variations with equivalence ratio.

Fig. 5. mT-SOFC performance at 800°C with hydrogen flowrate from 9.3 to 45.8 mL.min⁻¹.

Fig. 6. mT-FFC operating at 800°C with a model fuel-rich exhaust composition between equivalence ratios of 1.1 and 1.4.

Fig. 7. mT-FFC operating at 700°C with a model fuel-rich exhaust composition between equivalence ratios of 1.1 and 1.4.

Fig. 8. Comparison of the mT-FFC performance operating at 800°C in the model fuel-rich exhaust at equivalence ratios of 1.2, 1.3, 1.4 with the hydrogen baseline at equivalent electron potentials.

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