Micro-tubular Flame-assisted Fuel Cells for micro-Combined Heat and Power Systems

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ABSTRACT

Currently the role of fuel cells in future power generation is being examined, tested and discussed. However, implementing systems is more difficult because of sealing challenges, slow start-up and complex thermal management and fuel processing. A novel furnace system with a flame-assisted fuel cell is proposed that combines the thermal management and fuel processing systems by utilizing fuel-rich combustion. In addition, the flame-assisted fuel cell furnace is a micro-combined heat and power system, which can produce electricity for homes or businesses, providing resilience during power disruption while still providing heat. A micro-tubular solid oxide fuel cell achieves a significant performance of 430 mW cm^{-2} operating in a model fuel-rich exhaust stream.

Keywords: Micro-combined heat and power; Micro-tubular solid oxide fuel cell; Flame-assisted fuel cell; Solid-oxide fuel cell; Fuel-rich combustion

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1. INTRODUCTION

Heating systems including furnaces, hot water heaters and boilers are all based on combustion and heat exchanger systems that allow the chemical energy of a fuel, such as natural gas or propane, to be converted into heat. While these systems have become very efficient, there is an opportunity to utilize this same technology for power generation which will transform these heating devices into Combined Heat and Power (CHP) systems. Due to the low electricity demand in residential and small businesses, small scale CHP systems have been designated micro-CHP systems [1]. As these systems can operate on natural gas, propane, or wood they provide advantages compared to centrally distributed generation including resilience during power disruption, peak shaving and higher efficiency by avoiding transmission losses.

Despite the many options available for small scale power generation, Solid Oxide Fuel Cells (SOFCs) provide significant advantages for micro-CHP systems compared to their Internal Combustion Engine-based competitors because they are more-efficient, quieter, less polluting, and lacking moving parts, are potentially more reliable. Unfortunately, SOFC systems require complex fuel processing (due to a lack of a hydrogen infrastructure) and thermal management subsystems in order to operate at high temperatures (800-1000°C) for long periods of time. The fuel processing subsystem reforms readily available hydrocarbons, like methane and propane, into hydrogen and carbon monoxide (syngas) that can more readily be used directly in SOFCs. The thermal management subsystem brings the SOFC up to operating temperature and prevents thermal shock by maintaining the temperature during operation. A recent development that combines fuel processing and thermal management is the direct flame fuel cell (DFFC) in which a SOFC is placed in direct contact with a flame [2-5]. The flame acts as a partial oxidation reformer, reforming fuel to syngas and products of combustion, while operating on a wide

1 variety of solid, liquid and gaseous fuels. In addition, the flame simultaneously provides heat for
2 the SOFC operation and thus combines the thermal management and fuel reforming into a single
3 combustion process. Due to the simplicity of the setup, DFFCs have advantages over the more
4 traditional dual chamber SOFC (DC-SOFC) [6] and single chamber SOFC [7-10] including rapid
5 start-up and no sealing requirement [4,5,11-19]. Unfortunately, many studies have also revealed
6 DFFCs achieve low fuel utilization (<1%) which makes the heat to power ratio impractical and
7 the electrical efficiency low [4,5,13].

8 Instead of operating in direct contact with a flame, SOFCs could achieve higher fuel
9 utilization if they were integrated into the fuel-rich exhaust stream of conventional combustion
10 devices, creating a flame-assisted fuel cell (FFC). Specially, a SOFC can be integrated into a
11 furnace, boiler or hot water heater exhaust in order to create a micro-CHP system that can
12 potentially move the building off-grid. **Fig. 1** shows one example of a proposed residential size
13 flame-assisted fuel cell furnace for micro-CHP (FFF). This is one example of how FFCs can be
14 used to create a micro-CHP system. Natural gas is fed through the gas line to the in-shot burner
15 where the fuel is partially combusted. The fuel-rich exhaust moves through the tubular SOFCs
16 generating power and heat. Any remaining fuel is mixed with a secondary dilution air stream to
17 ensure complete combustion occurs prior to entering the flue. The exhaust gases then move
18 through the flue and exchange heat with the external air stream which is used to heat the
19 building. This novel furnace concept allows fuel-rich exhaust to generate power for the building.
20 The electricity generated has immediate use in powering the furnace blower, running a
21 refrigerator or being stored for later use.

22 The feasibility of the FFF concept was assessed in this study by first investigating the
23 exhaust composition of the fuel-rich combustion of methane gas, which is the primary

constituent of natural gas. The electrochemical behavior of a micro-tubular SOFC (mT-SOFC) [20-24] operating in a gas stream with the same composition and temperature as the combustion exhaust was analyzed. The mT-SOFC power curve, OCV and polarization were determined while operating in a model exhaust stream.

2. EXPERIMENTAL

2.1 Combustion Characterization

Fig. 2 is a schematic of the combustion characterization chamber. Methane was chosen as the fuel for the mT-SOFC. The flow rate of methane was fixed at 10 L min⁻¹ with the air flow rate varying in order to obtain the proper equivalence ratio. The equivalence ratio (ϕ) is defined as,

$$\Phi = \frac{n_{fuel} / n_{air}}{n_{fuel}^S / n_{air}^S}$$

where n_{fuel} and n_{air} are the molar flow rates of fuel and air respectively. Similarly, n_{fuel}^S and n_{air}^S are the molar flow rates of fuel and air for a stoichiometric reaction. Thus, an equivalence ratio of 1 represents a stoichiometric reaction and equivalence ratios greater than 1 are fuel-rich. The flow rate of methane and air was regulated by mass flow controllers and LabView software. A syringe was used to capture the combustion exhaust and direct it into a gas chromatograph (GC) for analysis. K-type thermocouples were used to measure the flame and the exhaust temperatures in the combustion apparatus. For the fuel-rich combustion of methane studied in this work, the exhaust composition is given by the following equation,

where a, b, c, d and e are the moles of hydrogen, carbon monoxide, carbon dioxide, water and nitrogen in the fuel-rich exhaust. Other exhaust components concentrations were small (<0.2%)

and are not included here. The GC measured the volume percent of each of the dry exhaust components at different equivalence ratios in order to balance the reaction and determine the flow rate of each exhaust component to the fuel cell.

2.2 Fuel Cell Fabrication and Characterization

An anode supported SOFC (AS-SOFC) was prepared by extrusion of the anode and wet-powder spraying of the electrolyte and cathode. Yttria-stabilized zirconia, YSZ, (Tosoh), NiO + YSZ (60:40 w/w, J.T.Baker) and LSM ((La_{0.8}Sr_{0.2})_{0.95}MnO_{3-x}) + YSZ (Fuel Cell Materials, 50:50 w/w) were used as the electrolyte, anode, and cathode materials, respectively. The anode was extruded and then sintered at 1000°C for 4h. The sintered anode has an internal diameter of 2.4mm and an outer diameter of 3.2mm. The YSZ was then spray deposited onto the anode surface using a spraying gun and then fired at 1400°C in air for 4h. The sintered electrolyte was 6µm thick. LSM + YSZ was deposited similarly and then sintered at 1100°C for 2h to form the complete fuel cells with a cathode layer (area: ~2.2cm²).

The I-V (current–voltage) method with the 4-probe technique was used to investigate the electrochemical behavior of the mT-SOFC. The open circuit voltage (OCV), power density and 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. Hydrogen at a flow rate of 48 mL min⁻¹ was first used to conduct the IV cell polarization tests and characterize the performance. The same test was repeated with a ‘model fuel’ that simulated the fuel-rich exhaust composition obtained from the combustion characterization tests. The exhaust was found to consist primarily of N₂, H₂, CO, and CO₂. Four separate mass flow controllers regulated the flow of N₂, H₂, CO, and CO₂ into a mixing chamber prior to going into the fuel cell. LabView data acquisition software was used to

control the mass flow controllers and thermocouple. The fabricated mT-SOFC was sealed onto the end of a steel tube using a ceramic adhesive. The steel tube was connected to the mass flow controllers and mixing chamber. The 'model fuel' representing the furnace exhaust is regulated by the mass flow controllers into the mixing chamber and then fed through the mT-SOFC. The mT-SOFC, which was sealed to the steel tube, was heated in a tubular furnace at a rate of 5°C per minute up to the operating temperature of 800°C.

3. RESULTS AND DISCUSSION

The rich flammability limit for the experimental apparatus was found to be at an equivalence ratio, ϕ , of ~1.4, which is the richest conditions that can be sustained for gas phase reactions without a catalyst. Other studies have confirmed that slightly higher equivalence ratios can be obtained for the rich flammability limit of methane fuel, but the results obtained ultimately depend on the experimental apparatus [25]. Fuel-rich exhaust ($\phi > 1$) composition was assessed as the equivalence ratio was varied between 1 and 1.4. **Fig. 3** reveals that the concentration of hydrogen and carbon monoxide, which can be used directly as fuel in mT-SOFCs, increase at higher equivalence ratios. The figure clearly shows a decrease in O₂ concentration as the stoichiometric point ($\phi = 1$) is reached, meaning that more fuel is combusted and O₂ is consumed. After passing stoichiometry, the concentration of fuels such as H₂ and CO increase because insufficient O₂ is available for complete combustion. The results, which are comparable to thermodynamic predictions [26], confirm that the highest fuel concentration occurs at the rich flammability limit with 12.4% H₂ and 8.7% CO. This indicates that more than 21% of the dry exhaust can be utilized as fuel in the mT-SOFC.

In addition to the availability of fuel, the experiment also confirmed that methane combustion achieved relevant temperatures for SOFC operation. The flame temperature was

1 1046°C with the exhaust temperature well above 800°C 10cm downstream, even without any
2 insulation on the combustion chamber. These operating temperatures indicates that traditional
3 SOFC materials, such as YSZ, which is already commercially available, can be utilized for this
4 system.

5 The fabricated mT-SOFC operating on H₂, the optimal fuel for SOFC operation, achieved
6 a peak power density of 652 mW cm⁻² at a fuel utilization of 49.3%. The power density is
7 comparable to other SOFCs with LSM cathode, but improvements in the fuel cell microstructure
8 are needed to further improve the fuel utilization. **Fig. 4** depicts the mT-SOFC operating with the
9 same exhaust composition found during the combustion test, creating the first micro-tubular
10 flame-assisted fuel cell (mT-FFC). The model exhaust was made to simulate an equivalence ratio
11 of 1.4 and had a total flow rate of 216 mL min⁻¹ with 12.4% H₂, 8.7% CO, 7.6% CO₂ and 71.3%
12 N₂. Hydrogen and carbon monoxide are fuels that participate directly in the electrochemical
13 reaction with the following reactions at the anode.

15 The CO₂ and N₂ do not participate in the reaction and dilute the fuel. The electrochemical
16 reaction of oxygen at the cathode is as follows.

18 As shown, the mT-FFC achieved a peak power density of 430 mW cm⁻² at a fuel utilization of
19 29.1%. The fuel utilization achieved in this study is 2 orders of magnitude higher than that
20 reported for a DFFC [4,5,13]. In the same study [13], the definition of fuel utilization is given
21 and will not be repeated here. This significant breakthrough is a result of separating the flame
22 from the anode surface, which allows the fuel generated by the partial oxidation of methane to be

utilized. Despite the fact that the combustion kinetics are much faster than electrochemical kinetics, the ability to separate the fuel cell from the combustion process allows for more fuel cell surface area to be used per unit of volumetric flow rate. Improvements in the fuel cell microstructure and a better matching of the fuel flowrate to surface area are expected to improve fuel utilization, meaning that the 29.1% achieved under the fuel-rich exhaust could be much higher. To ensure complete fuel utilization in the furnace, a catalytic combustor is used with the dilution air stream to ensure complete combustion of the fuel stream after passing through the fuel cells as well as maximum heat recovery by the furnace.

4. CONCLUSIONS

The significance of this study is that current combustion technologies including furnaces, boilers, hot water heaters, lanterns and stoves among others, can operate with a SOFC in fuel-rich exhaust to generate power. The high fuel utilization achieved indicates that practical micro-CHP devices could be constructed with this technology. Although pure hydrogen is the ideal fuel, significantly diluted hydrogen and carbon monoxide are enough to generate significant power. The FFF concept represents one example of how this technology could be employed for the next generation of heating devices which will generate power each time the furnace is in use, providing high system efficiency and promoting grid independence. The advantage of the system is that it does not drastically alter the existing furnace, but improves upon it by adding the benefits of micro-CHP.

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GLOSSARY

CHP – Combined heat and power

DC-SOFC – Dual chamber solid oxide fuel cell

DFFC – Direct flame fuel cell

FFC – Flame-assisted fuel cell

LSM – Lanthanum strontium manganite

mT-FFC – micro-tubular flame-assisted fuel cell

mT-SOFC – micro-tubular solid oxide fuel cell

OCV – Open circuit voltage

SC-SOFC – Single chamber solid oxide fuel cell

SOFC – Solid oxide fuel cell

YSZ – Ytria stabilized zirconia

Figure 1

Figure 2

Figure 3

Figure 4

FIGURE CAPTIONS

Figure 1: Residential size flame-assisted fuel cell furnace for micro-CHP (FFF) concept.

Figure 2: Combustion characterization apparatus.

Figure 3: Exhaust composition as the equivalence ratio is varied between 0.8 and 1.4.

Figure 4: mT-FFC operating at 800°C on methane exhaust at an equivalence ratio of 1.4.