A Thermally Self-Sustaining Miniature Solid Oxide Fuel Cell

Jeongmin Ahn, Paul Ronney*, Zongping Shao, Sossina Haile

Dept. of Mechanical & Materials Engineering, Washington State Univ., Pullman, WA
Dept. of Aerospace & Mechanical Engineering, Univ. of Southern California, Los Angeles CA College of Chemistry & Chemical Engineering, Nanjing Univ. of Technology, Nanjing, PRC
Materials Science and Chemical Engineering, California Institute of Technology, Pasadena, CA

Abstract

A thermally self-sustaining miniature power generation device was developed utilizing a single-chamber solid oxide fuel cell (SOFC) placed in a controlled thermal environment provided by a spiral counterflow "Swiss roll" heat exchanger and reactor. With the single-chamber design, fuel/oxygen crossover due to cracking of seals via thermal cycling is irrelevant and anode coking is practically eliminated. Appropriate SOFC operating temperatures were maintained even at low Reynolds numbers (Re) via reaction of the fuel cell effluent at the center of the Swiss roll. Both propane and butane fuels were examined. Extinction limits and thermal behavior of the integrated system were determined in equivalence ratio - Re parameter space and an optimal regime for SOFC operation was identified. SOFC power densities up to 420 mW/cm² were observed at low Re. These results suggest that single-chamber SOFC's integrated with heat-recirculating reactors may be a viable approach for small-scale power generation devices.

Keywords: Solid Oxide Fuel Cells; Swiss roll; single chamber; heat recirculation

1 - INTRODUCTION

It is well known that hydrocarbon fuels contain nearly 100 times more energy per unit mass than lithium-ion batteries, thus devices converting of fuel to electricity at better than 1% efficiency represent improvements in portable electronic devices and other battery-powered equipment [1]. At small scales, however, heat and friction losses become increasingly significant, thus devices based on existing macroscale designs such as internal combustion engines may be impractical. Microscale power generation devices using no moving parts may prove more feasible and offer manufacturing advantages. Consequently, many groups have considered heat-recirculating or "excess enthalpy" reactors first studied 30 years ago [2, 3] for thermal management and thermoelectric, piezoelectric or pyroelectric devices, having no moving parts, for power generation. In heat-recirculating reactors, by transferring thermal energy from the reaction products to the reactants without mass transfer (thus dilution of reactants), the total reactant enthalpy (sum of thermal and chemical enthalpy) is higher than in the incoming cold reactants and therefore can sustain reaction under conditions (lean mixtures, small heating value fuels, large heat losses) that would extinguish without recirculation. Therefore, reactor designs such as the counter-current, spiral "Swiss roll" heat exchanger and reactor may be ideally suited to microscale power generation applications.

Fuel cells offer a convenient means of generating electric power from conventional fuels and may also be well suited to microscale applications. Solid oxide fuel cells (SOFC’s), in particular, are attractive because they can be used with readily storable hydrocarbon fuels. Unlike like proton exchange membrane (PEM) fuel cells, SOFC’s can use hydrocarbons directly and do not require pre-reforming to H₂ prior to utilization. Rather, reforming to H₂ and CO can be performed in situ by partially oxidizing the hydrocarbon fuel on the anode surface of the cell itself. Fuel arrives at the anode, where it reacts with oxygen ions from the electrolyte, thereby releasing electrons (e⁻) to the external circuit. On the other side of the fuel cell, oxygen is fed to the cathode, where it supplies the oxygen ions (O²⁻) for the electrolyte by accepting electrons from the external circuit. The electrolyte conducts these ions between the electrodes, maintaining overall electrical charge balance. The flow of electrons in the external circuit provides useful power.

Typically, SOFC’s are used in a “dual chamber” configuration in which the fuel and oxidizer streams are sealed off from one another, posing both manufacturing and geometric constraints. The high operating temperatures of SOFCs renders such devices highly susceptible to thermal shock. Furthermore, seals are susceptible to cracking due to thermal cycling and chemical activity with the reactant streams, which can then lead to crossover between the fuel and oxidizer streams. Additionally, the high temperatures and strongly reducing environment on the anode side may lead to coking on the anode surface.

Because of these issues, recently Hibino et al [4] developed a “single chamber” SOFC in which both the anode and cathode are exposed to a premixed fuel-oxidizer mixture. Highly
selective catalysts are employed on both the anode and cathode surfaces. The single chamber configuration greatly simplifies geometric constraints on SOFC systems, eliminates issues related to sealing failures and reduces coking tendency.

While single chamber SOFCs are capable of operation at relatively low temperatures as far as SOFCs are concerned, temperatures in excess of 400˚C are still required. These high temperatures suggest that large heat losses and perhaps reaction quenching will occur in small scale devices, however, our previous work [5, 6] has shown that Swiss roll reactors can reduce quenching issues at low Re. Consequently, the objective of this work is to assess the feasibility of utilizing a single chamber SOFC in conjunction with a Swiss roll reactor for self-sustained thermal management at the low Reynolds numbers that would be encountered in a microscale device. A single-chamber SOFC is placed immediately upstream of the center of a Swiss roll reactor. Appropriate single chamber SOFC operating temperatures are maintained via reaction of the fuel cell effluent at the center of the reactor.

2 - APPARATUS AND PROCEDURES

Experiments were performed by placing a single chamber SOFC, aligned parallel with the gas flow direction, in a 3-turn, macro-scale, spiral, counterflow Swiss roll reactor (Figure 1), constructed from 0.6 mm thick Boron-Nitride ceramic sheets aligned and bonded using 904 Zirconia Ultra Hi-Temp ceramic adhesive. The outside dimensions of the reactor are approximately 5 cm wide by 5 cm deep by 3 cm tall. The gap-width for each inlet and exhaust channel is 3 mm. The top of the reactor is sealed with approximately 3 mm of fibrous ceramic blanket, backed by 3 mm aluminum plates, secured with ceramic adhesive. The fresh fuel-air mixture is plumbed through a manifold attached to the inlet of the Swiss roll. An electrically-heated Kanthal wire wrapped around a ceramic post located at the center of the reactor is used for ignition.

The single chamber SOFCs were constructed using a dual dry pressing and have a stacked geometry, consisting of a Ni+SmCeO₂ (Ni+SDC) anode cermet of approximately 7mm diameter, a samaria doped ceria (SDC) electrolyte with a thickness of approximately 50 mm, and transition metal perovskite cathode. The fuel cell area was approximately 0.7 cm². Further details on the fuel cell construction are presented elsewhere [7].

The reactor was instrumented with thermocouples located at the center and in each inlet and exhaust turn (seven total). Commercial mass flow controllers were used to regulate the flow rate of fuel and air through the reactor. LabView data acquisition software was used to record the response of each thermocouple and to control the mass flow controllers. Tests were performed by placing the SOFC in the inlet turn closest to the center of the Swiss roll, and sustaining a propane-air oxidation reaction at the center of the reactor. Silver paste was used to connect gold wires to both the anode and cathode sides of the cell. The wires were then insulated within the blanket and terminated outside the reactor test stand, where they were connected to a Keithley 2420 sourcemeter measuring current and voltage drop.

3 - RESULTS

The lean and rich extinction limits and thermal behavior of the ceramic Swiss roll were thoroughly mapped prior to SOFC testing. Extinction limits were determined by starting from a steady burning state and decreasing or increasing the fuel concentration with the igniter off. Self-sustained reactions with a bare platinum foil catalyst could be maintained within the Swiss roll at Reynolds numbers as low as 2. Furthermore, propane-air mixture compositions ranging from equivalence ratios of approximately 0.2 to 50 could be burned and a range of temperatures from approximately 75 C to 1300 C could be sustained. Measurements performed in an electrically heated tube furnace indicate that the single chamber SOFC’s being used in these experiments require an operating temperature ranging from 400˚C – 600˚C and a fuel-rich environment with a fuel to oxygen ratio close to 2. It was therefore determined that the ceramic Swiss roll could provide more than adequate thermal management for SOFC use.

First recognizing that a temperature gradient exists across each channel of the Swiss roll, SOFCs were tested with both the anode side and the cathode side facing the inner most side (hotter side) of the first inlet turn (from the center) of the Swiss roll. Polarization curves for each configuration are shown in Figure 2. Results are shown for a temperature immediately upstream of the fuel cell of 480˚C. C₃H₈O₂ = 1:2, and Re = 65. Similar behavior was observed over a range of temperatures. Noticeably better performance is obtained when the cathode is positioned facing the hotter wall of the first inlet turn.

Figure 1 - Ceramic Swiss roll reactor in experimental test stand with top plate removed.
SOFCs were then tested with both propane and butane as fuel. A polarization curve obtained with C\textsubscript{4}H\textsubscript{10} is shown in Figure 3. Results are shown for a Reynolds number of 80, a C\textsubscript{4}H\textsubscript{10}/O\textsubscript{2} ratio of 1:2, and a temperature (immediately upstream of the fuel cell) of 555 °C, which are the conditions yielded the best performance for this cell. Also, these results (and subsequent figures reported below) were obtained with the cathode side of the cell facing the hotter wall of the first inlet turn of the Swiss roll. A peak power density of 260 mW/cm\textsuperscript{2} was recorded at T = 520˚C and Re = 77. Similar results were also obtained at similar conditions with C\textsubscript{3}H\textsubscript{8}.

Figure 2 - Comparison of polarization curves for SOFC at T = 480˚C, C\textsubscript{3}H\textsubscript{8}/O\textsubscript{2} = 1:2, and Re = 65 with either the anode side or cathode side facing the inner wall.

Figure 3 - Polarization curve for SOFC at T = 555 C, C\textsubscript{4}H\textsubscript{10}/O\textsubscript{2} = 1:2, and Re = 80.

The behavior of peak power density as a function of mixture composition for a fixed temperature immediately upstream of the fuel cell (T=550°C) is shown in Figure 4 and as a function of temperature for fixed mixture composition (C\textsubscript{4}H\textsubscript{10}/O\textsubscript{2} = 1:2) in Figure 5. Note that the peak power density of SOFC varies by approximately 10% over the range of temperatures shown, indicating that the performance of this fuel cell is somewhat temperature dependent. The full polarization curves corresponding to this data (not shown) indicate that the current density at which peak power occurs does not change dramatically with temperature. Note also that temperature is strongly coupled to the reactant flow rate through the Swiss roll and therefore that SOFC may exhibit a dependence of peak power density on gas flow rate. The peak power density for SOFCs is sensitive to mixture composition and decreases as the fuel to air ratio decreases (i.e. less rich, closer to stoichiometric). Again, similar results were also obtained with C\textsubscript{3}H\textsubscript{8}.

Figure 4 - Peak power density for SOFCs with C\textsubscript{4}H\textsubscript{10} fuel as a function of mixture composition at T = 550˚C.

Figure 5 - Peak power density for SOFCs with C\textsubscript{4}H\textsubscript{10} as a function of temperature for C\textsubscript{4}H\textsubscript{10}/O\textsubscript{2} = 1:2.

Additional tests were performed using an improved transition metal perovskite cathode material [8]. A polarization curve obtained with this cathode is shown in Figure 6. Again, the cathode side of the cell faced the hotter wall of the first inlet turn of the Swiss roll. Peak power density was about 420 mW/cm\textsuperscript{2} for this cathode material. Figure 7 shows that the behavior of peak power density as a function of mixture composition for a fixed temperature immediately upstream of the fuel cell (550°C) is similar to previous results shown in Figure 4. Note that the peak power density for the SOFC is again sensitive to mixture composition and decreases as the fuel to air ratio decreases (i.e. less rich, closer to stoichiometric).
Figure 6 - Polarization curve for SOFC with new cathode at $T = 550^\circ C$, $C_3H_8/O_2 = 1:1.54$, and $Re = 85$.

Figure 7 - Peak power density (mW/cm$^2$) for SOFC with new cathode as a function of mixture composition at $T = 550^\circ C$.

4 - CONCLUSIONS

Experiments performed at low Reynolds numbers indicate that an integrated electric power generation system consisting of single chamber SOFCs placed in a Swiss roll reactor with a controlled thermal environment provided by the reaction of the fuel cell effluent at the center of the reactor is feasible. The detailed mapping of both thermal and extinction limit behavior of a ceramic Swiss roll in $(Re, \Phi)$ parameter space revealed that appropriate operating conditions for a single chamber SOFC could be maintained via self-sustained reaction. Single chamber SOFC's were tested with propane-air and butane-air mixtures over Reynolds numbers ranging from 40 to 100 and $C_3H_8/O_2$ ratios ranging from 1.47 to 2.59. Tests were performed by placing the fuel cells immediately upstream of the center of the Swiss roll and generating heat via the reaction of the fuel cell effluent at the center of the reactor. Peak power densities of up to 420 mW/cm$^2$ were recorded. The performance of both types of SOFCs tested in the Swiss roll was similar to that obtained in a tube furnace with electric resistance heating [8, 9]. Superior performance was obtained when the cathode side of the SOFC faced the hotter wall of the inlet channel. Peak power density was found to be dependent on temperature within the range over which power was produced, however, performance was much more strongly dependent on mixture composition over this range of temperatures.

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