ABSTRACT

This paper examines the behavior of a miniature tubular anode-supported SOFC at the limits of complete fuel utilization. Fuels include H2, CO and a 3:1-H2:CO mixture, selected to represent syngas. Construction of the NiO/8YSZ anode support, 8YSZ electrolyte, cathode and experimental apparatus are described. Current vs. voltage plots for fuel flow rates ranging from 0.6 to 6 sccm show the affects of fuel depletion near limiting currents. I-V plots are also used to investigate air leak rates and oxidation of Ni metal in the anode support. Measured electrical efficiencies are found to depend strongly on the operating conditions of the fuel cell and minute air leaks into anode channel. These leaks are quantified from open circuit voltages. Fuel composition, fuel flow, and operating voltage are found to influence the overall electrical efficiency. Because of air diffusing into the anode channel and the water gas shift reaction (CO + H2O ↔ CO2 + H2), syngas yields higher efficiencies than pure H2. Experimental results are compared with results of a thermodynamic model, which predicts the maximum theoretical electrical efficiency as a function of operating voltage.

INTRODUCTION

Commercial viability of fuel cells depends on producing electrical power more cheaply and reliably than current technologies. To this end, many investigators have focused on increasing the power density. High power densities reduce needed materials, and therefore lower initial costs: the SECA goal of $400/kW is often cited. Nonetheless, the overall cost of fuel cell operation depends on both the initial cost and operating costs. Direct fuel costs, as reflected in electrical efficiency, comprise the bulk of operating costs. Low operating costs are essential to fuel cell commercialization. Because SOFCs are fuel flexible and operate on reformed hydrocarbons, they are especially promising for low cost production of electric power (1). However, we believe electrical efficiencies greater than 60% must be achieved before widespread use of fuel cells may be anticipated (2,3). Moreover, we expect commercial SOFCs to be operated in a manner that minimizes operating cost by maximizing electrical efficiency ηe. Therefore, understanding the behavior of SOFCs at high electrical efficiency is essential. The electrical efficiency is defined as,

\[ \eta_e = \frac{P_{\text{net}}}{\sum_i n_i \Delta H_i} \]
where $P_{\text{total}}$ is total electrical power, $\dot{n}_i$ is the inlet fuel flow (mol/s), $i$ is the fuel species, $N$ is the number of fuel species, and $\Delta H_i$ is the enthalpy for complete oxidation of species $i$ at operating temperature.

This investigation focuses on predicting and measuring electrical efficiencies with fuels representative of general in-situ hydrocarbon reforming in SOFCs. An anode supported SOFC was constructed and operated to find electrical efficiencies as a function of operating voltage $V_{\text{cell}}$ and inlet fuel flow rate for H$_2$, CO, and syngas. Although syngas composition varies depending on the hydrocarbon source, a 3:1 H$_2$:CO ratio was used in this investigation. Fuel flow rates were sufficiently low to allow the cell to approach the limiting current $i_{\text{limit}}$, as defined by complete fuel utilization, $\eta_f = 100\%$. The limiting current for H$_2$ or CO oxidation is defined as,

$$i_{\text{limit}} = 2F \frac{dn}{dt},$$

where $2F$ is the number of Coulombs per mole and $dn/dt$ is the flow rate (mol/s). From Eq. 2 it can be shown that a 1 standard cm$^3$ per minute flow (scm) of H$_2$ or CO gives a limiting current of $i_{\text{limit}} = 143.5$ mA. The empirical results of our test cells are compared with the predictions of the thermodynamic model. The model itself is described elsewhere (4). Previous investigations with numerical models show that the electrical efficiency of a SOFC is strongly dependent on the operating voltage of the cell (4,5). Typically, peak electrical efficiency is predicted at operating voltages around $V_{\text{cell}} = 800$ mV and fuel utilization greater than $\eta_f = 90\%$.

**EXPERIMENTAL**

**SOFC Fabrication**

The SOFCs tested were miniature, tubular anode-supported cells with the cathode on the exterior of the tube. The tubular configuration was chosen for these experiments because the ratio of the seal area to the active cell area is much smaller than with small planar cells, so that gas-tight cells could be tested at the extremely low fuel flow rates required. Figure 1

![Diagram of SOFC](image-url)

**Figure 1.** Tubular anode-supported SOFC (left) and cut-away view showing fuel flow through the anode channel (right). The assembly is positioned in a tube furnace with a thermocouple. Fuel flow and electrical loads were varied to investigate SOFC current-voltage behavior.
(left) shows the fuel cell installed in the fuel cell test fixture. The outside diameter of the SOFC was 1.15 cm and the length of the tube segments was about 2.7 cm. The tubular anode support was traditional NiO/8YSZ cermet with a wall thickness of about 0.15 cm. The electrolyte was 8YSZ and the cathode was porous platinum. Both the electrolyte layer on the anode support and the cathode covering the electrolyte are visible in Fig. 1. The width of the cathode band was about 1.4 cm, making the active area of the cell about 5.0 cm².

The extruded anode support was made from a mixture of 8 mol% yttria-stabilized zirconia powder (Tosoh) and black nickel oxide powder (Novamet). Binders and water were added to these powders, and the mixture was extruded through a die at 4000 psi and air-dried. Next, the tube was bisque-fired at 1250°C for about an hour and cut into segments. The electrolyte was applied to the bisque-fired anode-support segments by vacuum slip casting. The electrolyte and anode support tubes were then co-fired at 1550°C for 4 hours. The sintered electrolyte film was about 30 µm thick, reasonably dense, with some closed porosity and a few small cracks. As the final step, a porous platinum cathode band was painted around the electrolyte and fired at 1000°C for 1 hour.

**Cell Assembly**

The cell test fixture was fabricated from high Ni-Cr alloy fittings. The fixture design is shown on the right side of Figure 1. An Inconel tube, 0.64 cm diameter by 46 cm long, was used to supply fuel to the anode chamber and serve as the anode current collector. The far end of the tube was capped with a stationary RA-601 high alloy fitting (Rolled Alloys) with an annular slot to center the SOFC test tube. A corresponding RA-601 bushing, with a minimal sliding clearance with respect to the OD of the Inconel tube, was attached to the other end of the SOFC tube. A small amount of silver paste was applied between the metal end fittings and anode support of the SOFC to ensure good electrical contact. Finally, the end seals were completed by applying vitreous sealing glass (Schott 8422). A layer of sealing glass was also applied to the band of exposed electrolyte not covered by platinum cathode. A silver wire (not shown) was wrapped around the length of the cathode to serve as the cathode current collector. The assembly was kept in compression by means of a 30 cm long ceramic sleeve inserted between the sliding bushing and a steel compression spring external to the test furnace. The cells were tested inside a horizontal tube furnace (Thermolyne F21135). The sealing glass was melted to make the seals gas-tight by momentarily bringing the assembled fixture to about 875 °C prior to lowering the cell to the final operating temperature.

**Cell Testing**

Fuel gas was supplied to the cell by a MKS 1479A mass flow controller (MFC). The MFC was capable of delivering a maximum of 10 standard cubic centimeters per minute (scm) with a resolution of about 0.05 scm. Fuel flowed into the sealed anode chamber through two small transverse holes in the Inconel tube near the fixed end. Excess fuel and exhaust gases flowed back along the anode channel, and out of the cell through the small, 75 µm, gap between the sliding bushing and the Inconel tube. Average gas velocities in the anode channel (between the fuel supply tube and anode support tube) ranged from 0.19 and 1.15 cm/s for fuel flows of 1 to 6 scm. In order to operate the cell in the region of the limiting current, fuel flow rates were necessarily low (less than 6 scm). As gas was exhausted through the gap in the bushing, average gas velocities were much higher, ranging from 4 to
24 cm/s. These velocities were high enough to prevent air from diffusing back into the cell. Fuel flow inside the anode channel was laminar for all operating conditions. The pressure inside the anode chamber was maintained at slightly above atmospheric pressure. The pressure drop to the atmosphere was less than 20 mm H2O as measured by a bubbler attached to the fuel supply tube. Current and voltage generated by the cell was measured with a Chroma 63103 electronic load. A Labview computer program adjusted the electrical load, recorded I-V and temperature data, and operated the MFC.

For the low fuel flow rates used in this investigation, the fuel cell approached steady state rather slowly. Prior to the experiment, I-V curves with different rest times were taken. Repeatable I-V curves were attained with a 10 second rest time. We also found that longer rest times were required for lower flow rates. Typically, the load was adjusted in 5 mA increments with a rest time of 10 seconds between each measurement. A 60 second rest time was used for fuel flows of 1 sccm or less for each current increment. The internal volume of the fuel supply tube and anode channel acted as a fuel reservoir with a total volume of about 5.8 cm³, so this entire volume needed to equilibrate, in order to reflect the new operating conditions. An important advantage to this experimental design, however, was that pressures inside the anode channel were always close to atmospheric pressure, and varied little with changing gas flow rate. Therefore, the measured voltages were not influenced by the fuel flow rate, but rather by the equilibrium partial pressures of the gas species present. Of course, the tradeoff was long settling times and very slow I-V scans.

After positioning the cell assembly in the tube furnace, and setting the end seals, NiO in the NiO/YSZ anode support was reduced in-situ to Ni metal by flowing 10 sccm of pure H2 through the anode channel at 825°C for 24 hours. I-V curves were obtained with H2, CO, and syngas as a function of flow rate. The various fuel flow rates were held constant during each I-V scan while air-flow over the cathode was maintained at 1400 sccm. After switching fuels the cell was purged with the new fuel for 30 minutes prior to taking I-V scans. A thermocouple was positioned about 1 cm from the cathode to measure the cell temperature.

RESULTS AND DISCUSSION

Figure 2 shows the experimental I-V curves for H2, CO, and syngas for differing fuel feed rates. In all cases the temperature was maintained at 825°C and airflow into the tube furnace was 1.4 standard liters per minute (slpm). Currents are shown for comparison with fuel flow. The top panel in Fig. 2 shows the I-V curves for 1 to 6 sccm pure H2. The 6 sccm I-V curve is approximately linear from open circuit to 100mV since excess fuel is available. A shallower slope in the I-V curve (proportional to the area specific resistance, ASR) is observed for currents above 200 mA. The ASR is 7.1 Ω-cm² at current below 200 mA and 5.6 Ω-cm² for currents above 200 mA. Importantly, the ASR and power density are fuel cell specific and do not influence the electrical efficiency (4,5). At lower fuel flow the cell reaches the limiting current, which is shown as a dotted line for each flow rate. For fuel flow ranging from 1 to 3 sccm, the I-V curves begin to roll off to zero near the limiting current as expected.

Surprisingly, the I-V curves continue beyond the limiting current, thus exceeding the limiting current and theoretical electrical efficiency. This is explained by electrochemical oxidation of Ni metal in the anode support due to locally oxidizing conditions, which occurs when the
gas phase fuel in the anode channel becomes depleted. Thus, the Ni metal acts as a secondary "fuel" extending the I-V curves and increasing the electrical efficiency beyond the predicted values. To support this hypothesis, I-V curves were taken on pure helium. Next, a fully reduced anode supported SOFC was weighed then operated at a steady electrical load for 24 hours while purging the anode channel with pure He. After operating on He, the SOFC was cooled and reweighed. A weight gain of 250 mg was measured. Moreover, the weight gain was consistent with the amount of O₂ added to the cell electrochemically (see Eq. 2). Details of the phenomenon are the subject of a forthcoming paper. We believe that the role of anode support oxidation at high fuel utilization has not been previously unreported.

The middle panel of Fig. 2 shows I-V curves for pure CO. A relatively high flow of CO, 6.63 sccm, produced a nearly linear I-V curve. At lower flows the cell was able to exhaust the fuel supply as shown by the limiting currents (shown as dotted lines). As in the H₂ case the I-V curve shows a steep rolloff near the limiting current. The cell showed slightly diminished open circuit voltages as flow was reduced.

The lower panel of Fig. 2 gives the I-V curves for syngas (3:1 H₂:CO). As shown, a 6 sccm fuel feed provides excess fuel. The shape of the I-V curves is consistent with those for H₂ in the top panel. However, the open circuit voltages of the I-V curves in the top panel and those in the lower panel of Fig. 2 differ. The open circuit voltage of H₂ drops as the flow of

![Figure 2. I-V curves for different fuels, H₂ top panel, CO middle panel, and syngas (3:1 H₂:CO) in the lower panel.](image-url)
H₂ is reduced (top panel Fig. 2). This behavior is consistent with a leak in the cell either in
the fixture or through the electrolyte itself. Since the anode channel is at a slight positive
pressure, convective leaks of fuel from the cell cannot explain the loss in open circuit voltage
at low flows.

Air leaking into the anode channel through small pores and cracks in the electrolyte can be
expected to reduce the open circuit voltage by increasing the H₂O partial pressure and
decreasing the H₂ partial pressure. The open circuit voltage is related to these partial
pressures by the Nernst potential, which is defined as

\[ E_r = \frac{-\Delta G}{2F} + \frac{RT}{4F} \ln(P_{O_2}(c)) + \frac{RT}{2F} \ln \left( \frac{P_{H_2}(a)}{P_{H_2O}(a)} \right) \]  

where \( \Delta G \) is Gibbs free energy of the reaction, \( H_2 + \frac{1}{2}O_2 \rightarrow H_2O \), \( F \) is Faraday's constant,
\( R \) is the gas constant, \( T \) is temperature Kelvin, \( P(a) \) and \( P(c) \) are the gas pressures in bar at
the anode and cathode respectively.

Figure 3 plots the open circuit voltages as a function of H₂ flow
into the anode channel (also shown in the top panel of Fig. 2). Measured open circuit voltages are
shown as squares. The solid line represents the Nernst potential resulting from a diffusive air leak
into the anode channel. To calculate the Nernst potential three
assumptions are made. First, O₂ transported into the anode channel
reacts with H₂ to form water vapor. Second, air leaks are the only source
of O₂ since no O₂⁻ ions are transported through the electrolyte at
open circuit. Third, pressure changes in the anode channel due to changes in fuel flow are
less than 20 mm H₂O (0.002 bar) and therefore inconsequential. Therefore, the last term in
Eq. 3 varies with the leak rate. Least squares fitting of Eq. 3 to the measured open circuit
voltages yields an air leak rate of 0.87 scm, as shown in Fig. 3. This leak rate corresponds
to H₂O generation rate of 0.36 scm.

In contrast to the H₂ open circuit voltages shown in Fig. 3, the CO-H₂ mixture exhibits nearly
constant open circuit voltage until the flow is reduced to 1.0 scm (lower panel Fig. 2). The
water gas shift (WGS) reaction explains this behavior. When CO and H₂O are present at the
anode the WGS reaction (\( CO + H_2O \leftrightarrow CO_2 + H_2 \)) increases the H₂ partial pressure, and
reduces H₂O partial pressure. The WGS reaction is fast and immediately proceeds to
equilibrium (5). As a consequence, the open circuit voltage is sustained with air leaking in.
Of course, the flow of CO into the cell must be greater than the amount of H₂O generated by
the leak or the voltage will fall. The lower panel of Fig. 2 shows a rapid drop in the I-V
curve when the flow of syngas is reduced below 1.5 scm. At 1.5 scm syngas the flow of
CO (0.38 scm) is about equal to the H₂O generation rate (0.36 scm). We conclude that the
presence of CO allows a SOFC operating on syngas to maintain higher open circuit voltage and achieve higher electrical efficiencies than a cell operating on pure H₂ when leaks are present.

Figure 4 illustrates the measured electrical efficiencies from I-V curves in Fig. 2 together with efficiencies predicted with the thermodynamic model (solid lines). Efficiencies are presented "as measured" and are not corrected. The highest efficiencies occur at very low fuel flow rates and at currents near the limiting current $i_{\text{limit}}$. Generally, the measured efficiency increases with decreasing flow rate. The limiting current for each fuel flow rate is shown with a grey circle. One would expect the measured efficiencies to be less than the efficiencies predicted by the thermodynamic model. Nevertheless, the measured efficiencies exceed predictions in the region of interest, i.e., high fuel utilization. Leaks in through the electrolyte act to both reduce open circuit voltages and overall electrical efficiency. Leaks cannot explain the I-V curves exceeding the limiting current or the electrical efficiency exceeding the theoretical limit.

The top panel in Fig. 4 shows results for pure H₂. At a 6 sccm flow of H₂ the efficiency is low ($\eta_e = 20.6\%$ at 511 mV) because the current that can be drawn by the SOFC is too small to consume all of the fuel, i.e., most of the H₂ flows out the exhaust. At 3 sccm flow of H₂ the peak electrical efficiency increases considerably, $\eta_e = 30.0\%$ at 515 mV. The highest measured electrical efficiency $\eta_e = 43.4\%$, at 572 mV occurs at the limiting current of the 1.5 sccm flow (shown with crosses). A peak electrical efficiency of 58.3% near 800 mV is predicted from the model. Thus, measured efficiencies with pure H₂ are considerably lower than the theoretical maximum.

Consider the middle panel of Fig. 4: peak theoretical efficiency is only 51% yet CO clearly outperforms pure H₂. A likely explanation of this difference is that it is more difficult to leak air into the anode when the small pores and cracks contain a mixture of air, CO and CO₂ than it is when air is mixed with H₂ and H₂O. The leak rate (using the least squares

Figure 4. Measured (markers) and theoretical (solid lines) electrical efficiencies as a function of operating voltage.
fit analysis used for Fig. 2) for CO is 0.51 sccm air.

Figure 4 (middle panel) follows the trend of reduced electrical efficiency for greater flow rates. The highest efficiencies were achieved for CO flow rates of 1.45 sccm (triangles) and 0.81 sccm (crosses) where $\eta_e = 49\%$ at 732 mV and $\eta_e = 50.5\%$ at 778 mV respectively (efficiencies in excess of the limiting currents were not considered). In both cases, the observed efficiencies were very near the theoretical efficiency of the cell $\eta_e = 51.1\%$. At still lower flow rates, leaks reduce the open circuit voltage and electrical efficiency.

The lower panel of Fig. 4 shows the measured electrical efficiencies of a syngas mixture (3:1 H$_2$:CO). With the exception of 6 sccm, open circuit voltages are higher than those for equivalent flows of H$_2$ and electrical efficiencies are improved for operating voltages above 800 mV. At operating voltages below 600 mV higher flow rates, show good agreement with the theoretical electrical efficiency. At 1.0 sccm and 1.5 sccm the measured efficiencies have a double peak appearance, where the lower voltage peak is due to oxidation of the anode support.

Figure 5 compares measured, corrected and theoretical electrical efficiency for 1 sccm of syngas. I-V and efficiency curves are also shown in Fig. 2 (lower panel) and Fig. 4 (lower panel). The measured efficiencies are shown as squares and the corrected efficiencies are shown as circles. Measured and corrected values beyond the limiting current are not shown. Consider the lower panel of Fig. 2, at a 6 sccm flow rate the open circuit voltage of the cell is 1017 mV and all of the I-V curves are nearly parallel for operating voltages above 700 mV. Moreover, one would expect the open circuit voltage to remain unchanged in the absence of air leaks since the pressure of fuel gases is constant in the anode channel. It follows that the

![Figure 5. Measured, corrected and theoretical electrical efficiencies for a 1 sccm flow of syngas (3:1 H$_2$:CO).](image)

I-V curve should be adjusted to account for air leakage. Adjusting the measured voltages of the 1 sccm I-V curve by 76.5 mV results in a corrected I-V curve, which lies on top of the 6 sccm I-V curve. Of course the two I-V curves diverge before reaching the limiting current. As can be seen in Fig. 5, the corrected data does a reasonable job of matching the thermodynamic model except that the peak efficiency occurs at a lower cell voltage.
CONCLUSIONS

We have investigated SOFC performance under conditions necessary for very high electrical efficiency. These conditions require flow rates on the order of 0.2 sccm/cm² in the experiment. Operating conditions for high electrical efficiency are very different from the large excess fuel conditions frequently used to reach high power densities. As fuel is depleted the performance of a fuel cell becomes sensitive to small gas leaks, which are inconsequential at high rates of fuel flow.

Based on the present work, we conclude that:

1. Near theoretical electrical efficiencies are possible in practical devices using CO-H₂ mixtures. Nevertheless, small gas leaks can significantly impact the efficiencies of the fuel cell. Therefore, practical devices attaining high electrical efficiency will require both gas tight seals and an impermeable electrolyte.

2. At low operating voltages near the limiting current, Ni in the anode support is oxidized to form NiO. Oxidation of Ni metal complicates interpretation of the experimental data near limiting currents. Since anode oxidation artificially inflates the apparent cell efficiency.

3. Lower operating temperatures offer substantial benefits, including higher electrical efficiencies and use of common metals for fuel cell construction.

4. Based on the results of this investigation, attaining electrical efficiencies of 60% appears extremely challenging.

REFERENCES

1. Fuel Cell Handbook (6th Ed.), Technical Report {DOE/NETL-2002/1179}, National Energy Technology Laboratory, Morgantown, WV, (2004).

2. W. G. Coors, in Fifth European Solid Oxide Forum Proceedings, J. Huijsmans, Editor, p. 602, European Fuel Cell Forum, Switzerland, (2002).

3. G. Coors, R. Sidwell, and F. Anderson, in Sixth European Solid Oxide Fuel Cell Forum Proceedings, M.Mogensen, Editor, p. 117, European Fuel Cell Forum, Switzerland, (2004).

4. R. Sidwell, and G. Coors, J. Power Sources, accepted, (2004).

5. R. J. Kee, H. Zhu, D. G. Goodwin, R. W. Sidwell, and W. G. Coors, in these Proceedings.