V.8 High Temperature Fuel Cells for Co-Generation of Chemicals and Electricity

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Objectives

- Determine the thermal self-sustainability, temperature gradients, electrical output, product composition, efficiency, and syngas productivity of a methane electrochemical partial oxidation (EPOx) reactor.
- Develop methods to avoid coking, and prove that excellent stability against coking can be achieved during long-term operation.
- Explore the use of alternative anode materials in order to eliminate coking with methane and other hydrocarbons and also allow redox cycling.
- Evaluate the technical and economic viability of the proposed technology based on the above information.

Accomplishments

- Showed that stability and coke-free direct-methane solid oxide fuel cell (SOFC) operation is promoted by the addition of small amounts of CO_2 or air to the fuel stream.
- The operation range for coke-free operation is greatly increased by replacing the thin nickel yttria-stabilized zirconia (Ni-YSZ) anode support with a ceramic support, including segmented-in-series stacks.
- Stable coke-free operation in natural gas was achieved by using a ceramic-anode-supported SOFC.
- Demonstrated current interruptions of up to 8 minutes in methane with no permanent coking or change in cell performance.
- EPOx operation was demonstrated at 750°C that yielded 0.9 W/cm^2 and a syngas production rate of 30 sccm/cm^2, with reaction product composition close to equilibrium during the early stages of cell testing.
- The stability of methane conversion was improved via the addition of a reforming catalyst to the SOFC anode.

Introduction

In the second year of this Phase I project, we have further studied direct-methane and direct-natural-gas operation of SOFCs. It was demonstrated that SOFCs can simultaneously produce high electrical power density and high-quality syngas. A new issue with poor reforming stability of the Ni-YSZ anode/catalyst was discovered, and the initial solution of adding a catalyst material was demonstrated.

Combined generation of electricity and syngas has significant potential economic advantages. That is, when SOFCs become cost-effective for electricity generation, the syngas becomes a low-cost by-product. This could provide an important new route to low-cost hydrogen and gas-to-liquid fuels. From another perspective, the ability to sell both electricity and chemicals increases the value of the SOFCs, improving their prospects for commercialization.

Approach

Extensive electrical testing of anode-supported SOFCs with methane and simulated natural gas fuel were done in combination with gas chromatograph and mass spectrometer measurements of reaction products for a range of conditions. While these were single-cell tests, the cell area and current were large enough to achieve partial oxidation stoichiometry ($O^{2-}/CH_4 \approx 1$) for reasonable fuel flow rates. Cell stability was tested versus additions of H_2O/CO_2 to the methane, barrier layers, and for ceramic-anode-supported cells.

Detailed modeling was carried out in collaboration with Colorado School of Mines, providing detailed predictions of gas composition gradients within the anode and anode flow field. The work focused on the effect of anode barrier layers on overall cell/stack performance and changes in the gas composition within the Ni-YSZ anode that influence anode coking. Most model input parameters were quantitatively established by structural evaluation of the SOFCs and barriers combined with calibration experiments performance on the SOFCs prior to methane testing.

Results

In order to demonstrate EPOx in a larger-area multiple-cell configuration, a segmented-in-series (SIS)-SOFC module was operated directly with methane under EPOx conditions. The segmented-in-series modules can produce a total of 8 W at 800°C in humidified hydrogen, corresponding to ~650 mW/cm^2 [1]. These devices consist of thick-film SOFC layers on a ceramic (partially-stabilized zirconia) anode support. For the EPOx experiments, a Ru-CeO_2 catalyst material was applied to the inner surfaces of the SIS-SOFC tube that was operated at 750°C. Stack power density was 325 mW/cm^2 at 750°C and 600 mW/cm^2 at 800°C, similar to the values obtained for the same stack with hydrogen fuel. Mass spectrometer exhaust gas measurements at 750°C with an O^{2-}/CH_4 ratio of ≈1 showed very good methane conversion of ~90% with the primary products being CO and H_2 with a small amount of CO_2.

We have tested direct-methane stability in SOFCs with (Sr,La)TiO_3 (SLT) ceramic anode supports. A series of methane stability tests were carried out at different current densities. Figure 1 shows the result in dry methane at 800°C. The current density was first maintained at 0.5 A/cm^2, and then decreased by 0.1 A/cm^2 and stability tested again for >8 hours. The cell was stable at the lowest current density tested, 0.1 A/cm^2. For comparison, Ni-YSZ-supported cells were not stable unless the current density was at least 1.0 A/cm^2. That is, the SLT-supported cells showed a much wider stability range than conventional SOFCs (even with barrier layers). This dramatic increase in the stability range is presumably due to the relatively thin Ni-containing active layer in these cells, combined with the thick SLT support layer that acts as a built-in barrier layer.

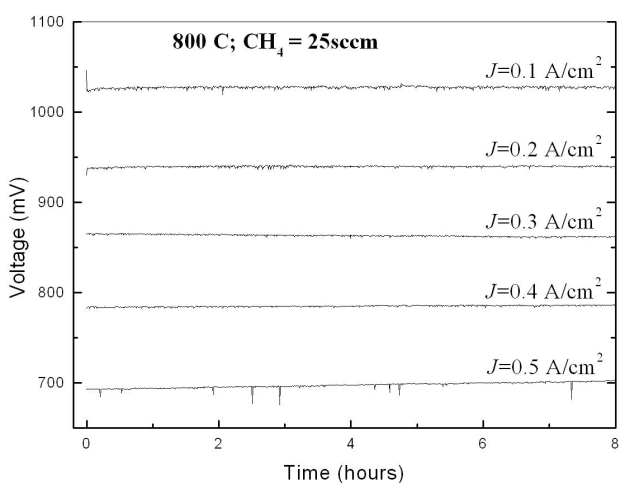

FIGURE 1. Measured Product Composition versus Time from an EPOx SOFC Reactor Showing a Gradual Decrease in Methane Conversion to Syngas over 35 Hours

An SLT-supported SOFC was tested in the "worst-case" natural gas mixture of 85% methane, 10% ethane, and 5% propane. The cell was stable over 72 hours. Figure 2 shows an image of this cell showing the Ni-YSZ active layer (bottom), dense YSZ electrolyte layer (middle), and the LSM-YSZ/LSM cathode layer (top). There was no coking observed on the active layer. Images from other areas of the anode support showed a SLT structure similar to that in Figure 2, with no evidence of coking. Furthermore, ceramic-supported SOFCs with thin Ni-based active layers have shown excellent redox stability, such that it would be possible to clean any carbon from the SOFC anode and anode compartment by periodically exposing to air. The ceramic-supported SOFCs are very similar to conventional Ni-YSZ anode-supported cells; thus, they could easily be substituted into conventional planar stacks.

Although our results have shown that SOFCs are stable during steady-state operation at a reasonable current density, it was not clear what would happen if there was a break in stack current. Thus, studies of the effects of different current interruption cycles on single SOFCs were carried out. Figure 3 shows a typical interruption test. After the cell reached steady-state operating on pure methane at 750°C, the current was abruptly stopped for 1.5 mins, and then abruptly increased back to 1.8 A/cm^2. The voltage returned to its initial steady-state value after briefly being higher than the original value. A similar result was obtained with a subsequent 6-min interruption. However, when the

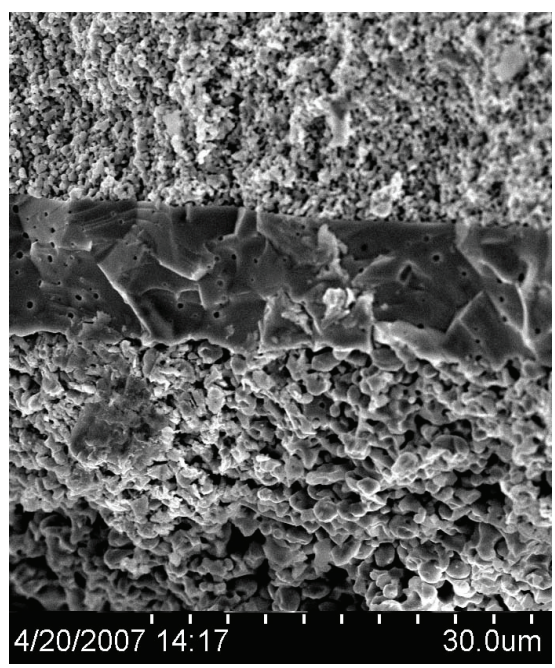

FIGURE 2. Cross Sectional SEM Image of the Active Region of the SLT-supported SOFC after Operation in Synthetic Natural Gas at 700°C

interruption time was increased to 10 mins, the voltage remained ~15 mV lower than before the interruption. These results suggest that although coking occurs when the cell is at open circuit, the early stage coking does not cause any permanent damage. Resumption of cell current actually etches carbon from the anode, returning the cell to its initial condition and performance. On the other hand, for a ≥10-min interruption, carbon buildup continues to a point where the carbon fills and then begins to expand anode pore cavities. The result is irreversible structural damage to the anode. The bottom line is that direct-methane SOFCs can survive several minutes without current, such that methane could be flushed from the cell prior to any damage.

Gas chromatography measurements have shown that the initial product gas composition closely approximates that expected from equilibrium calculations with >90% methane conversion. Figure 4 shows an example of the syngas output experimentally measured from a SOFC versus the O^{2-}/CH_4 ratio (varied by changing the SOFC current). The measurements were done during the early stages of operation, there was no barrier layer, and pure methane was the fuel. Also shown on the plot are the predicted equilibrium gas compositions. The measured gas composition is quite close to the equilibrium prediction. Furthermore, at a near-optimal O^{2-}/CH_4 ratio of 1.2, only ≈5% methane remains in the fuel stream and 2.4 moles of syngas are produced per mole of methane, very near the ideal ratio of 3. That is, the SOFC acts as a near-ideal partial oxidation reactor.

Figure 5 shows a plot that helps illustrate the efficacy of the SOFC as a dual electricity/syngas generator. In this case, the methane flow rate and oxygen ion current were varied together in order to maintain a constant O^{2-}/CH_4 ratio = 1.2. The plot shows the output power density and syngas production rate versus the methane flow and cell current. The syngas production rate increased linearly with the methane inlet flow rate. The power density curve shows the normal dependence on cell current density, with at peak power at 0.92 W/cm^2. This figure shows that it is possible to obtain ~0.9 W/cm^2 power output from the SOFC while producing a syngas output of ~30 sccm/cm^2. The power density is similar to state-of-the-art SOFCs operated at 750°C, whereas the syngas rate is comparable to the best ceramic membrane reactors, although these are typically operated at a higher temperature of 900°C [2, 3].

It is important to note that the data in Figures 4 and 5 were obtained during the early stages of SOFC

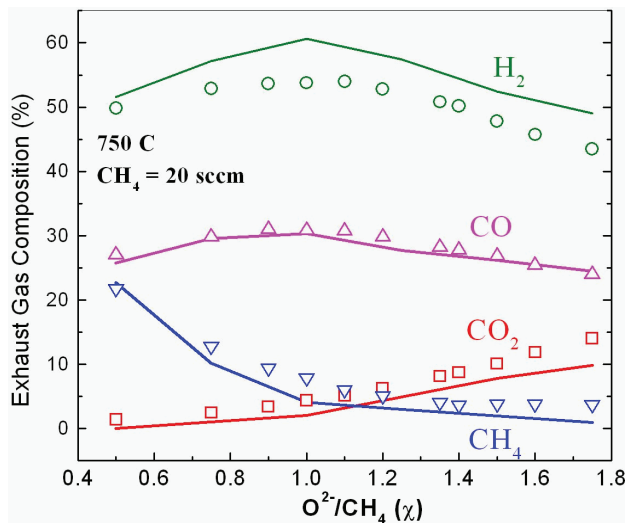

FIGURE 4. Measured Product Gas Composition (Data Points) and Equilibrium Values (Curves) versus Oxygen to Methane Ratio

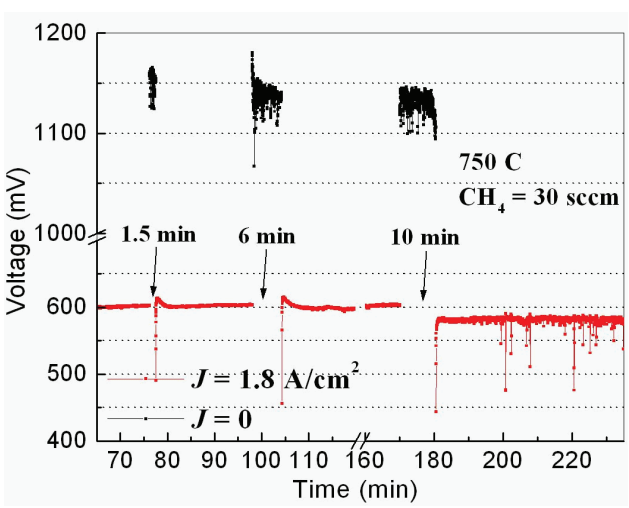

FIGURE 3. Effect of Current Interruptions on the Performance of a SOFC at 750°C on Methane Fuel

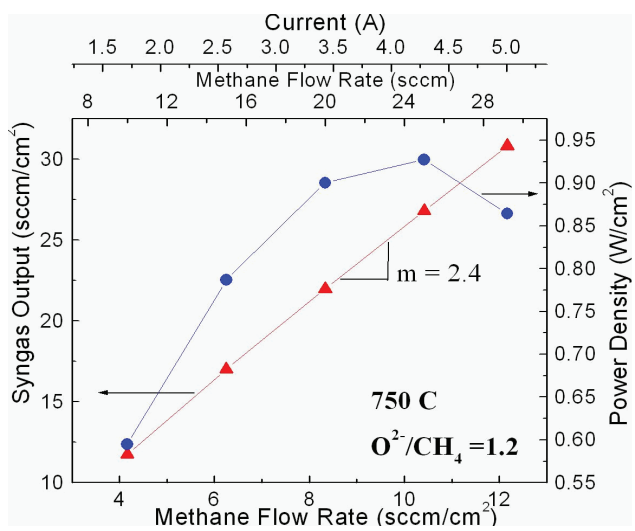

FIGURE 5. Syngas Output and Power Density versus Methane Flow Rate (and Cell Current) with the Ratio O^{2-}/CH_4 Maintained Constant at 1.2

operation. The methane conversion to syngas was found to decrease gradually with increasing operation time. That is, the amounts of methane, steam, and CO_2 in the exhaust increased, while CO and H_2 decreased. This occurred even while the SOFC was stable and the O^{2-}/CH_4 ratio was constant. This indicates that the reforming activity of the Ni-YSZ anode was decreasing with time, in agreement with recent results from David King's group at Pacific Northwest National Laboratory (see presentations at the Solid State Energy Conversion Alliance Review meeting, Fall 2006, Philadelphia). Note that reforming is necessary because the SOFC products are primarily H_2O and CO_2 – these must reform CH_4 in order to produce syngas. The Ni anodes have been thoroughly tested for carbon, so it is clear that the catalyst was not deactivated by coking.

Based on the above, the addition of catalysts to the SOFC anodes was investigated. Initial work with Rh-alumina catalysts applied directly to the SOFC anode showed much better product stability than the SOFC with no catalyst. More work is needed on catalyst testing to demonstrate the desired long-term stability. The prospects of finding an appropriate catalyst are good, since stable catalyst systems have already been developed for other types of methane reforming.

Conclusions and Future Directions

The above results demonstrate that direct-methane SOFCs can very effectively produce electricity while converting methane to syngas. Cell stability testing has continued to show ways to increase the stable operation range for SOFCs with methane fuel; a particularly important example is the ceramic-anode-supported SOFC, which shows excellent stability in both methane and natural gas. It was also found that SOFCs can survive current interruptions of several minutes without any damage.

A key area for future work is clearly to develop catalyst systems that provide stable long-term reforming activity and thus stable syngas production. To test this, stability tests of several hundred hours will be carried out. The tests will increasingly focus on $(Sr,La)TiO_3$-anode-supported single SOFCs and segmented-in-series SOFCs. Simulation work will continue in order to obtain more accurate predictions of gas composition and temperature gradients within the anodes of these ceramic-supported SOFCs, to help explain the stability results.

FY 2007 Publications/Presentations

1. Zhu, H., Colclasure, A.M., Kee, R.J., Lin, Y. & Barnett, S.A., Anode barrier layers for tubular solid-oxide fuel cells with hydrocarbon fuel streams. *J. Power Sources* **161**(1), 413-419 (2006).

2. Zhan, Z., Lin, Y., Pillai, M., Kim, I. & Barnett, S.A., High-rate electrochemical partial oxidation of methane in solid oxide fuel cells. *Journal of Power Sources* **161**(1), 460-465 (2006).

3. Huayang Zhu, Andrew M. Colclasure, Robert J. Kee, Yuanbo Lin, Scott A. Barnett, "Tubular solid-oxide fuel cells using either anode recycle or barrier layers," 7th European Solid Oxide Fuel Cell Forum, Edited by Ulf Bossel.

4. Scott A. Barnett, "Hydrocarbon reforming processes internal to solid oxide fuel cells" Hydrocarbon Resources Gordon Conference, Ventura, CA, January 2007.

5. Manoj Pillai, Yuanbo Lin and Scott A. Barnett, Huayang Zhu, Andrew M. Colclasure, and Robert J. Kee, Effect of Anode Barrier Layer and Hydrocarbon Fuel Composition On Solid Oxide Fuel Cell Stability, American Ceramic Society Conference, Daytona Beach, FL, January 2007.

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1. Pillai, M.R., Gostovic, D., Kim, I. & Barnett, S.A., Short-period segmented-in-series solid oxide fuel cells on flattened tube supports. Journal of Power Sources **163**(2), 960-965 (2007).

2. Sundmacher, K., Rihko-Struckmann, L.K. & Galvita, V., Solid electrolyte membrane reactors: Status and trends. Catalysis Today **104**(2-4), 185-199 (2005).

3. Bouwmeester, H.J.M., Dense ceramic membranes for methane conversion. Catalysis Today **82**(1-4), 141-150 (2003).