

Oxidation of Dry and Near-Dry Hydrocarbons at High Power Density Anodes

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Objectives

- Develop high-power density solid oxide fuel cell (SOFC) anodes capable of operating directly on as-received hydrocarbon fuels, thus reducing or eliminating the need for fuel processing and sulfur removal upstream of the fuel cell stack.

Key Milestones

- Control carbon formation and sulfur tolerance to enable stable cell operation on dry or near-dry methane and sulfur-containing natural gas at 700 to 800 °C.
- Fabricate and scale-up sufficiently strong, copper-containing cells containing an active interlayer designed to increase power density.
- Achieve improved power densities when operating on dry or near-dry methane and sulfur-containing natural gas at 700 to 800 °C.

Approach

GTI is developing methods for fabricating and testing copper-based cermet anodes, having an active interlayer between the anode support and the electrolyte. The copper component inhibits carbon and sulfur formation while maintaining high electronic conductivity. The active interlayer is targeted at improving power density without sacrificing sulfur tolerance or carbon inhibition. The interlayer design parameters include dimensions, particle sizes, porosity, pore sizes, and relative constituent amounts. Complete single cells, incorporating the anodes, are fabricated within the constraint of the low melting point of copper oxide. The project is obtaining data on electrochemical performance, carbon resistance, and sulfur tolerance, and conducting pre- and post-cell test surface analytic evaluation to understand cell performance. Cell testing is initially targeting intermediate power densities (>200 mW/cm²), low hydrocarbon fuel utilizations ($<15\%$), and relatively small cells (~ 3 cm²). The project is focused on 700 to 800 °C operation on methane and sulfur-containing natural gas at very low steam-to-carbon ratios, and possibly extending results to other hydrocarbon fuels.

Results

Significant performance stability for 150 to 300 hours or longer has been obtained when operating 2.8 cm² active area cells at 800 °C on dry CH₄. The stable cell operation shown in Figure 1 thus far requires cells with a relatively thick, 83μm, electrolyte and/or a relatively thin, 200μm, anode. The cells in Figure 1 were fabricated by standard dual tape-casting/wet impregnation methods and do not contain an active interlayer intended to increase power density. Post-test evaluation indicates that carbon forms, but it is sufficiently controlled to permit stable operation over the test period. To date, operation on dry methane at 800 °C with thinner (13μm) electrolyte and thicker ($\sim 600\mu$ m) anode cells has been much less stable.

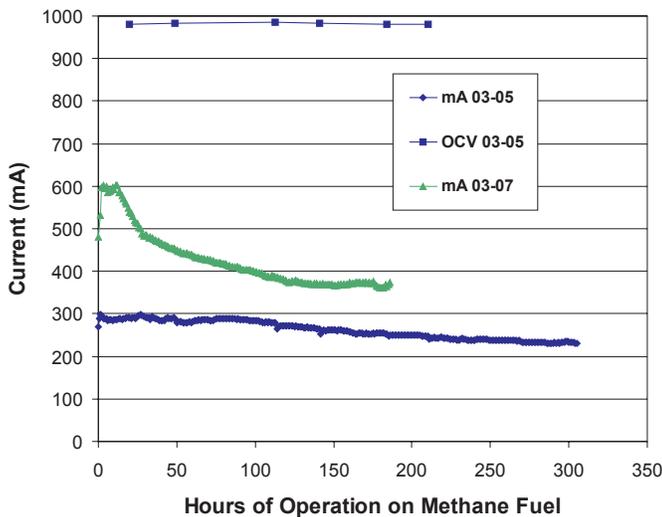


Figure 1. Performance of two cells on dry methane and 97% air/3% H₂O at 800C and 0.5V.

Multiple interpretations for the differences observed in cell-to-cell power density are possible, including differences in cell sealing effectiveness, cell contact resistance due to the quality and uniformity of cell components, and the performance of electrodes and/or electrolytes. These issues are under investigation.

As shown in Figure 2, stable operation could be obtained with 13m-thick electrolyte/~600μ-thick anode cells by adding 75ppm of sulfur compounds to dry CH₄. The addition of 75ppm of sulfur compounds (cell 03-09) greatly increased cell life compared with a similar test (cell 03-08) without the addition of sulfur. With the sulfur-containing composition, carbon formation was reduced much more than in other cell tests at 800 °C. The result suggests that the copper-containing anodes tolerate sulfur, and sulfur inhibits carbon formation. Previous GTI patents [1] have identified the sulfur tolerance of copper-containing electrodes. Sulfur is known to inhibit carbon formation via the Boudouard reaction under these conditions.

Experiments are underway to determine the influence of sulfur addition on power density. The low power density observed with the sulfur composition could be due either to the effect of sulfur, or differences in the cell/test configuration, as discussed above.

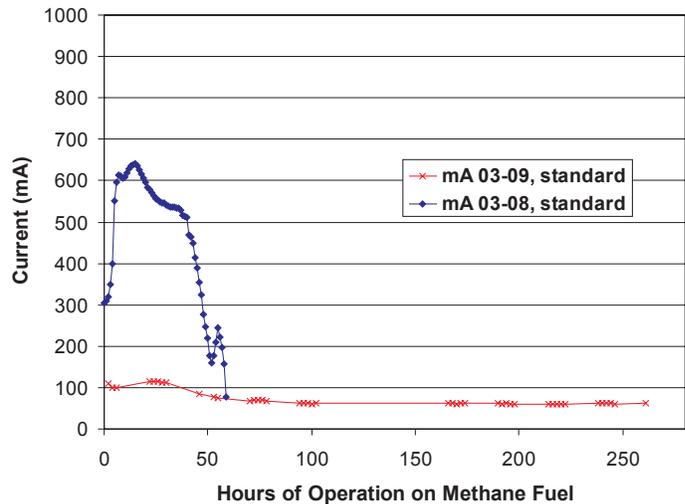
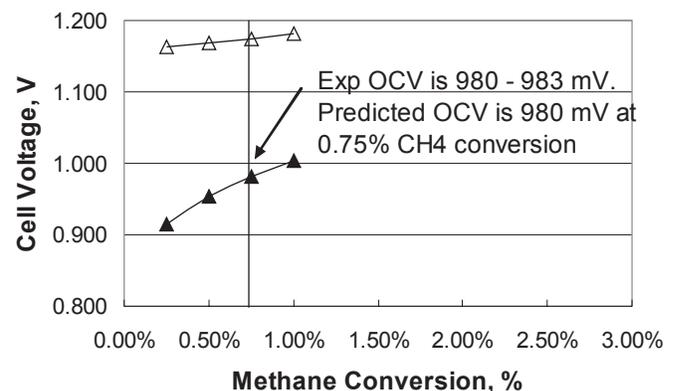


Figure 2. Comparison of cell operation on dry methane and methane with 75 ppm sulfur compounds at 800C and 0.5V.

Working with Technologix Corporation, GTI has performed preliminary equilibrium modeling of the open circuit voltage (OCV) of these systems, as shown in Figure 3. Assuming no mixed potential contribution, the experimental OCV for dry methane oxidation agrees closely with an OCV predicted on the basis of near-dry CH₄ conditions, and an initial low conversion of CH₄ by internal reforming, followed by oxidation of product H₂. The experimental OCV does not appear to agree well with an OCV predicted on the basis of direct oxidation of CH₄ by O²⁻.



- ▲ H₂+0.5O₂=H₂O : 1%H₂O,1%CO₂,bal CH₄
- △ CH₄+2O₂=CO₂+2H₂O : 1%H₂O,1%CO₂,bal CH₄

Figure 3. Comparison of predicted and experimental OCV for oxidation of methane at 800 °C. Darkened symbols refer to a reforming pathway, and open symbols refer direct oxidation.

Conclusions

Initial project results have identified cells and test conditions for controlling carbon deposition when operating on dry CH_4 at 800 °C, showed that copper-based cells operating on dry CH_4 may tolerate sulfur, and the sulfur addition may extend cell life by minimizing carbon formation, and have introduced an alternative potential mechanism for the electrochemical oxidation of dry CH_4 (and possibly other hydrocarbons) at 800 °C, based on an initial internal reforming step.

Continuing research will focus on fabricating stronger, larger area cells, testing higher power density cells containing an active interlayer, and understanding cell and test conditions that will further minimize carbon formation and increase performance uniformity. Discussions with several research groups are underway for possible coordination of efforts.

References

1. L. Marianowski, G. Anderson, E. Camara, "Use of Sulfur Containing Fuel in Molten Carbonate Fuel Cells," U.S. Patent No. 5,071,718, December 10, 1991.
L. Marianowski, G. Anderson, E. Camara, "Sulfur Tolerant Molten Carbonate Fuel Cell Anode," U.S. Patent No. 4,925,745, May 15, 1990.