

V.L.1 Development of Kilowatt-Scale Coal Fuel Cell Technology*

Steven S.C. Chuang (Primary Contact),
Felipe Guzman, Tritti Siengchum,
Azadeh Rismanchian, and Jelvehnaz Mirzababaei
The University of Akron
302 Buchtel Common
Akron, OH 44310-3906
Phone: (330) 972-6993
E-mail: schuang@uakron.edu

DOE Managers

HQ: Dimitrios Papageorgopoulos
Phone: (202) 586-5463
E-mail: Dimitrios.Papageoropoulos@ee.doe.gov
GO: Reg Tyler
Phone: (720) 356-1805
E-mail: Reginald.Tyler@go.doe.gov

Contract Number: DE-FC36-08GO0881114

Project Start Date: June 1, 2008

Project End Date: May 31, 2012

*Congressionally directed project

megawatt scale. A current density of 100 mA/cm² at 0.4 V was the initial target for demonstration of a coal-based SOFC.

FY 2011 Accomplishments

FY 2011 research focused on achieving the following milestones:

- Studied the generation of electric power in the coal-based SOFC using two types of solid carbon fuels: biomass-based coconut coke and bituminous Ohio #5 coke.
- Demonstrated that exposure to CO₂ streams increases the performance of Ni-based anode SOFCs during electrochemical oxidation of carbon.
- Synthesized a Cu-Ni/YSZ (yttria-stabilized zirconia) anode catalyst that exhibits higher resistance to deactivation due to SO₂ exposure, as compared to conventional Ni/YSZ anodes.



Introduction

Coal-based SOFCs produce electricity by direct utilization of solid carbon in coal. The use of solid carbon as fuel constitutes a highly desirable technology because of its high energy density (20 kW h/L) compared to methane (0.011 kW h/L), hydrogen (0.003 kW h/L) and diesel (9.8 kW h/L) at standard conditions (i.e., 1 atm and 273 K) [1]. Direct conversion of the chemical energy of carbon to electricity could reduce the complexities associated with fuel processing, facilitating the utilization of abundant carbon resources, and mitigating emission of pollutants (i.e., NO_x species). Coal-based SOFCs with all solid-state components offer significant advantages over molten hydroxide and molten carbonate coal-based fuel cells including (i) ease of stack assembly, and (ii) avoiding electrolyte degradation/corrosion [2]. The performance of the coal-based fuel cell is limited by the extent of contact between the solid carbon and the anode electrode, where the electrochemical oxidation reaction takes place. As a result, development of a highly active coal-based SOFC requires developing anode catalysts that exhibit high activity towards electrochemical oxidation of carbon in coal, and resistance to poisoning due to contaminants such as sulfur. The main objectives of this project are (i) improving the anode catalyst activity and durability, (ii) developing and refining the coal-based SOFC fabrication techniques, and (iii) testing a small-scale coal SOFC system. Successful development of this novel coal fuel cell technology will significantly enhance the energy security of the U.S. and improve the market penetration of fuel cells.

Fiscal Year (FY) 2011 Objectives

Develop a kilowatt-scale coal-based solid oxide fuel cell (SOFC) technology. The outcome of this research effort will form the technological basis for developing a megawatt-scale coal-based SOFC technology. Objectives for 2011 included the following:

- Investigate the effect of the type of solid carbon fuel on the ability to generate electric power in the coal-based SOFC.
- Determine the effect of the concentration of CO₂ on the performance of the coal-based SOFC.
- Develop anode materials that exhibit resistance to deactivation due to exposure to sulfur-containing species.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance

Technical Targets

This project will develop a technological basis for the scale up of power generation capability of a kW SOFC to

Approach

An experimental campaign was designed and implemented to (i) fabricate anode supported SOFCs comprising a Ni/yttria-stabilized zirconia (YSZ) anode, YSZ electrolyte, and YSZ/lanthanum strontium manganese oxide (LSM) cathode, and (ii) evaluate the voltage–current polarization plots (i.e., V-I curves) of the SOFCs at 750°C and 1 atm during testing in H₂, CH₄, CO₂, SO₂, and two types of solid carbon fuel (biomass-based coconut coke and bituminous Ohio #5 coke). Ohio #5 coke was produced by pyrolysis of Ohio #5 coal samples, as described in previous work [3]. The effect of the type of solid carbon fuel was studied by testing the fuel cell in batch mode with 10 g of each fuel, recording the fuel cell steady-state power output at a constant load. The SOFC performance was correlated with the structure and chemical composition of the carbon fuel, which was characterized by diffuse reflectance infrared fourier transformed spectroscopy (DRIFT) and X-ray fluorescence (XRF). The effect of CO₂ streams on the SOFC performance was studied by recording the steady-state V-I polarization plots in H₂ and Ohio #5 coke, and analyzing the composition of gases at the exhaust of the cell. The Ni/YSZ anode electrodes were modified by addition of copper in order to investigate the resistance to deactivation by sulfur poisoning. Cu-Ni/YSZ anode fuel cells were prepared by depositing a layer of copper (Cu⁰) on the surface of reduced Ni/YSZ cells, according to the electroless deposition method. The resistance of the Cu-Ni/YSZ anode to sulfur species was investigated by exposing a Cu-Ni/YSZ fuel cell to a H₂/He and CH₄/He streams containing SO₂ (1.0 vol%), operating the cells at a constant load. The fuel cells used in these studies were characterized by XRF, scanning electron microscopy (SEM), and electrochemical impedance spectroscopy (EIS).

Results

The generation of electric power in the coal-based SOFC was investigated using two types of solid carbon: biomass-based coconut coke and bituminous Ohio #5 coke produced by pyrolysis of Ohio #5 coal. Figure 1 shows direct use of biomass-based coconut coke in the SOFC produced a power density of 125 mW/cm² continuously at 750°C, while the power density with Ohio #5 coke fuel decreased from 50 to 2 mW/cm² after 15 h of testing. The decreased power density was attributed to low activity of Ohio #5 coke, which contains less functional groups and alkali metals as compared to biomass-based coconut coke. Figure 2 shows the DRIFT spectra of Ohio #5 coke and coconut coke, confirming the stronger characteristic infrared (IR) absorptions of saturated (2,927 cm⁻¹) and aromatic C-H bands (3,045 cm⁻¹), aromatic C=C band (1,607 cm⁻¹), and oxygenates present on the surface of coconut coke. The less intensive characteristic IR absorption of Ohio #5 coke was attributed to the removal of surface functional groups during pyrolysis of Ohio #5 coal. Pyrolysis of coal

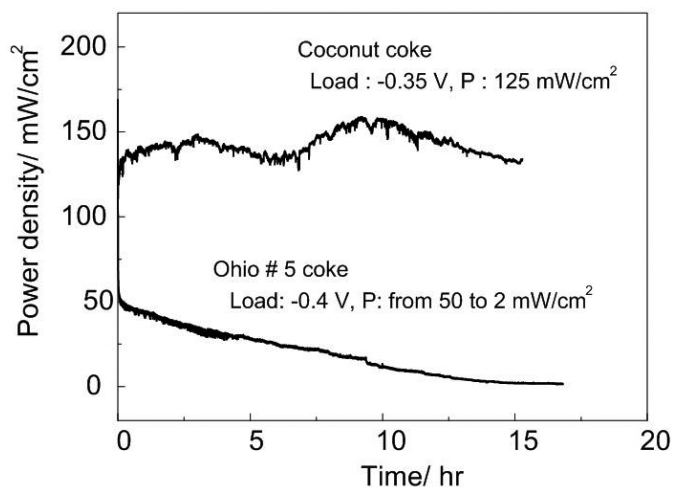


FIGURE 1. Fuel cell power output as a function of time recorded during operation in 10 g of biomass-based coconut coke and bituminous Ohio #5 coke.

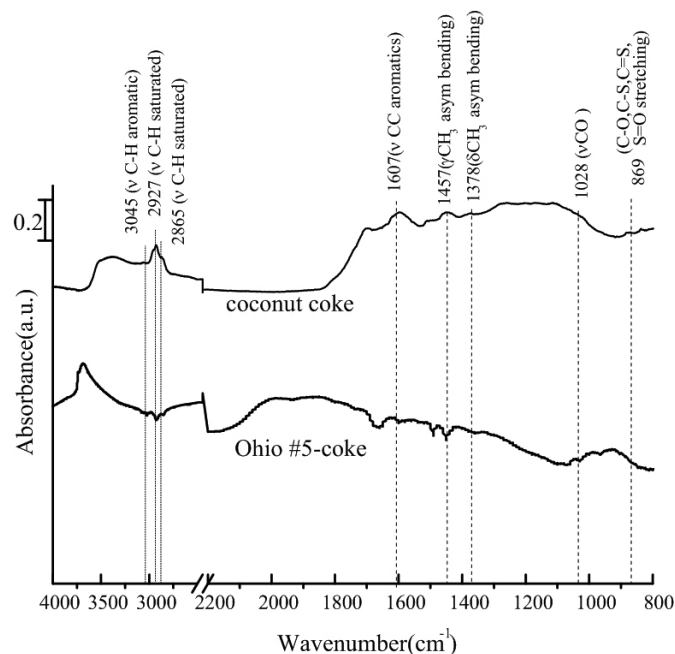


FIGURE 2. DRIFT spectra of Ohio #5 coke and biomass-based coconut coke.

caused the loss of surface functionality and heterogeneity through dehydrogenation, dealkylation, and oxidation reactions. XRF elemental analysis of Ohio #5 coke and coconut coke revealed the higher content of K in coconut coke with respect to Ohio #5 coke. The alkaline metals, e.g. Li, Na, and K, have been reported to catalyze gasification of carbon [4]. Thus, the solid carbon containing alkaline metals would be expected to be more active in gas-phase reactions than the carbon without catalysts. The high fuel cell performance observed during testing in coconut coke suggests that alkaline metals catalyzed the carbon

gasification to produce CO, which can be further undergo electrochemical oxidation by reacting with O^{2-} on the anode surface increasing power density. In contrast, the Ohio #5 coke lacked sufficient gasification activity, resulting in low rate of electrochemical oxidation.

Research studies conducted during FY 2011 provided experimental evidence of the improvement in the performance of Ni-based anode fuel cells in the presence of CO_2 streams. Figure 3 shows the voltage vs. current characteristics of a Ni/YSZ anode supported fuel cell at $750^\circ C$ in 10 g of low-ash carbon and a He/ CO_2 stream containing different concentrations of CO_2 (25-100 vol% CO_2). Increasing the CO_2 concentration from 25 to 75 vol% caused an improvement in the fuel cell performance of nearly 71%, which corresponded to maximum power density of 69 mW/cm^2 . The improvement on the fuel cell performance in the presence of higher CO_2 concentrations could result from electrochemical oxidation of CO produced by gasification reactions of the low-ash carbon and CO_2 (i.e., Boudouard reaction, $C + CO_2 \rightarrow 2CO$). The extent of the low-ash carbon gasification reactions, and their impact on the fuel cell energy efficiency will be further investigated in future studies.

Testing experiments demonstrated that Cu-Ni/YSZ anodes prepared by the electroless deposition of Cu onto Ni/YSZ anodes possess high electrochemical oxidation activity and resistance to deactivation by sulfur containing species. Figure 4 shows a plot of current density as a function of time for a Cu-Ni/YSZ and a Ni/YSZ anode fuel cell exposed to a CH_4/He stream (100 sccm, 50 vol% CH_4) before and after addition of 1 vol% SO_2 . The Cu-Ni/YSZ anode fuel cell produced a current density output of 0.45 A/cm^2 in CH_4/He . Addition of 1 vol% SO_2 resulted in a gradual decrease in the current density output until reaching 0.39 A/cm^2 (13% decay) after 15 min of operation. Further exposure to SO_2 did not cause noticeable changes

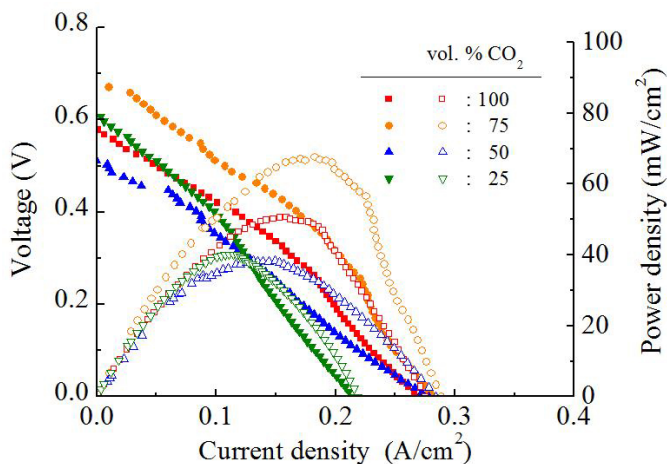


FIGURE 3. Voltage vs. current (closed symbols) and power vs. current (open symbols) characteristics of a Ni anode supported fuel cell at $750^\circ C$ in 10 g of low-ash carbon and a He/ CO_2 .

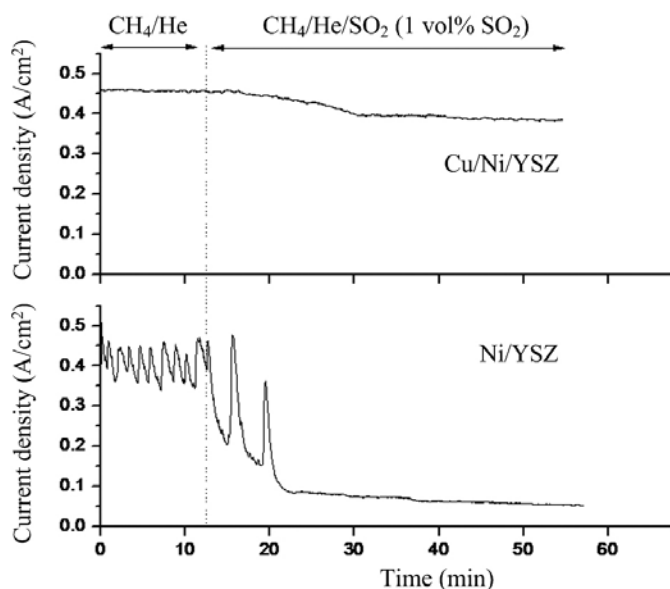


FIGURE 4. Current density as a function of time for a Cu-Ni/YSZ and a Ni/YSZ anode fuel cell exposed to a CH_4/He stream (100 sccm, 50 vol% CH_4) before and after addition of 1 vol% SO_2 .

in current density output, manifesting the resistance of the Cu-Ni/YSZ anode to deactivation by sulfur poisoning. Exposure of the Ni/YSZ anode fuel cell to the CH_4/He stream produced a fluctuating current density output with an average close to 0.4 A/cm^2 . The variation in the current density output could result from rapid formation of carbon deposits on the Ni/YSZ anode (i.e., coking). Addition of 1 vol% SO_2 resulted in a rapid decay in the fuel cell current density output, reaching 0.04 A/cm^2 (90% decay) after 8 min. XRD and XRF analysis of the Ni/YSZ fuel cells after the testing experiments (data not shown) revealed exposure to SO_2 resulted in formation of Ni_3S_2 on the anode surface. Formation of Ni_3S_2 on the Ni/YSZ anode fuel cell could reduce the number of sites available for reaction, resulting in significant losses in the fuel cell current density output. Unlike the Ni/YSZ anode, XRF and XRD spectra of the Cu-Ni/YSZ did not reveal the presence of sulfur-containing species. The absence of sulfur species could result from higher dissociation energy of sulfur species on Cu-Ni surfaces, as described in previous studies [5].

Conclusions and Future Directions

Studies conducted during fiscal year 2011 documented the effects of the chemical composition of solid carbon on the performance of the coal-based SOFC. Addition of CO_2 to Ni-based anode SOFCs was found to increase the gasification of carbon producing CO, which in turn can be electrochemically oxidized increasing the fuel cell power output. Electroless deposition of Cu onto Ni/YSZ anodes was found to improve the fuel cell resistance to sulfur containing species such as SO_2 .

Future studies will focus on:

- Refining the composition, structure, and thickness of the anode catalyst to obtain higher current densities and improved resistance to deactivation.
- Evaluating the long-term anode and cathode catalyst durability.
- Improving a coal injection and fly-ash removal systems for continuous operation for the coal-based SOFC in solid carbon fuels.

FY 2011 Publications/Presentations

1. Guzman, F., Singh, R., Chuang, SSC., *Energy & Fuels*. **2011**, 25, 2179.

References

1. Zecevic, S.; Patton, E.M.; Parhami, P., *Carbon* **2004**, 42, (10), 1983.
2. Nabae, Y.; Pointon, K.D.; Irvine, J.T.S., *J. Electrochem. Soc.* **2009**, 156, (6), B716.
3. Singh, R.; Guzman, F.; Khatri, R.; Chuang, S.S.C., *Energy & Fuels*. **2010**, 24, (2), 1176.
4. Li, C.; Shi, Y.; Cai, N., *J. Power Sources* **2010**, 195, (15), 4660.
5. Galea, N.M.; Knapp, D.; Ziegler, T., *J. Catal.* **2007**, 247, (1), 20.