

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

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Contract Number: DE-FC36-08GO0881114

Project Start Date: June 1, 2008

Project End Date: May 31, 2012

*Congressionally directed project

(B) Cost

(C) Performance

Technical Targets

This project will develop a technological basis for the scale up of power generation capability of a kilowatt SOFC to 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 2012 Accomplishments

- The source contributing to polarization loss is the capacitance of the Ni/YSZ anode, which suggests the necessity of improving anode and anode current collector conductivity.
- The exposure of the carbon SOFC to 7 mol% H₂O increases the maximum power density of the carbon fuel cell by 1.7 times during the continuous operation.
- The integration of individual fuel cells in series and parallel stacks achieved an open circuit voltage close to the expected Nernst potential.
- The efficiency of carbon SOFC operated with coconut coke was evaluated and the products were quantified.

Fiscal Year (FY) 2012 Objectives

To 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 2012 included the following:

- Identifying the sources contributing to polarization loss which limit the activity of the Ni/yttria-stabilized zirconia (YSZ) anode electrode.
- Demonstrating continuous operation of SOFC in solid carbon with additional H₂O.
- Integrating individual fuel cells in series and parallel stack.
- Evaluating the effect of fuel cell load on the formation of CO and CO₂, and the fuel cell efficiency on the SOFC operated in solid carbon.

Technical Barriers

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

(A) Durability



Introduction

The direct use of coal in the SOFC to generate electricity is an innovative concept for electric power generation. The coal-based SOFC could offer significant advantages: (i) minimization of oxides of nitrogen emissions due to the operating temperature range of 700-1,000°C, (ii) high overall efficiency because of the direct conversion of coal to CO₂, (iii) production of a nearly pure CO₂ exhaust stream for the direct CO₂ sequestration, and (iv) low investment and maintenance costs due to the simplicity of the process. This technology also promises to provide low-cost electricity by expanding the utilization of U.S. coal supplies and relieving our dependence on foreign oil.

A small-scale coal SOFC system including coal injection and fly ash removal parts will be fabricated. The main objectives of this project are (i) improving the anode catalyst structure, and the interface between electrodes and electrolyte, (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 bridge the gap between a fossil fuel-based economy and the future hydrogen-based economy.

Approach

An experimental campaign was designed and implemented with the objectives of: (i) measuring electrochemical impedance spectra of carbon SOFC at different direct current bias, (ii) evaluating the fuel cell performance characteristics in the presence of H₂O streams, (iii) quantifying the amount of CO and CO₂ produced from operation of carbon SOFCs at different operating current densities, and (iv) evaluating the efficiency of the carbon fuel cell in flowing He and CO/He. A procedure was developed for the large-scale fabrication of anode-supported SOFCs using tape casting and screen-printing techniques. Tape casting formulations containing NiO and YSZ powders, organic additives, and different amounts of pore formers (i.e., organic fillers that can be burned completely without leaving ash residues) were prepared and tested. Fuel cells fabricated by this approach were characterized by X-ray fluorescence, scanning electron microscopy, and electrochemical impedance spectroscopy. The effect of H₂O on the performance of the fuel cell was studied by recording the steady-state voltage–current polarization plots (i.e., V-I curves) in H₂ and carbonaceous fuels, and analyzing the composition of gases at the exhaust of the cell. Low ash carbon fuels, i.e., coconut coke, were tested during continuous operation of the fuel cell at a constant load. Quantification of CO and CO₂ was achieved by means of a calibration factor obtained from gas chromatography and mass spectrometry calibrations.

Results

Identifying the Sources Contributing to Polarization Loss

A Ni/YSZ fuel cell was tested in a spring-loaded reactor comprising an alumina tube, a steel plate serving as cathode current collector, and a Cu tube serving as anode current collector. Pellets of pyrolyzed Ohio #5 coal were loaded between the Ni/YSZ anode and Cu tube anode current collector. The fuel cell was tested at 750°C and 1 atm in flowing 100 sccm He. Electrochemical impedance spectra of the fuel cell was recorded with a potentiostat unit (1,400 cell test Solartron) from 1 MHz to 0.01 Hz with signal amplitude of 10 mV at various direct current density biases, shown in Figure 1(a). A direct current density bias of 0 A/cm² exhibits two overlapping arcs. Increasing the direct current density bias caused a significant growth in the high frequency arc until eventually concealed the low frequency arc, as observed in the spectrum at 0.09 A/cm². Changing the direct current bias did not cause significant variations in the intercept of the high frequency arc (160-250 Hz) with the X-axis, indicating that the total ohmic losses remained constant. The rise in

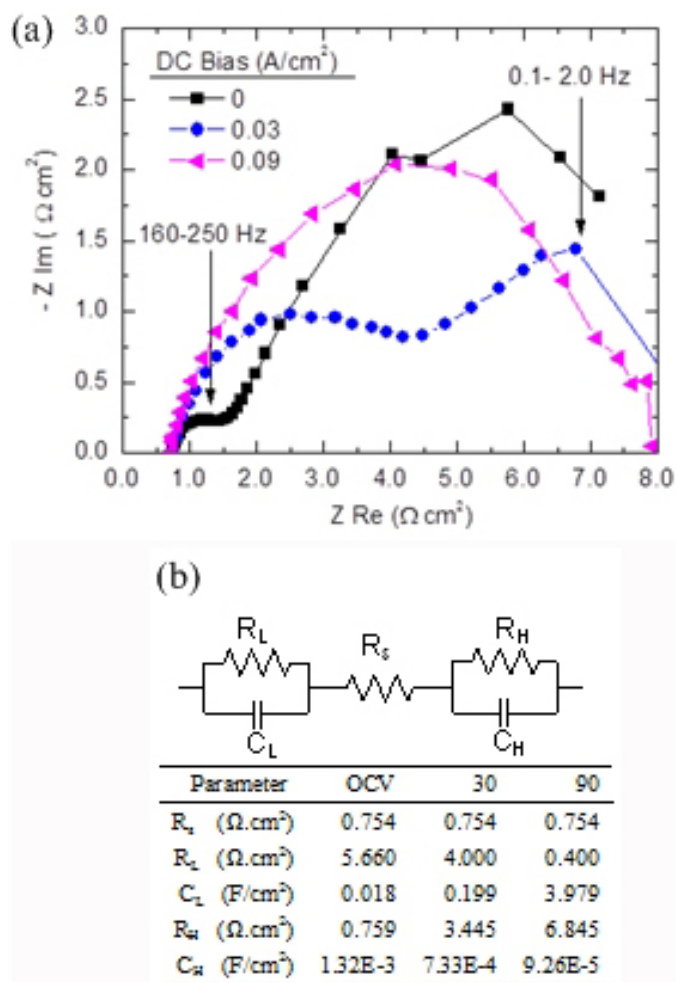


FIGURE 1. (a) Impedance spectra collected at a direct current density of 0.09, 0.03, and 0 A/cm²; (b) Parameters calculated from the equivalent circuit and the experimental impedance spectra of fuel cell with Ohio #5 coke fuel

the height of the high frequency arc can be attributed to the larger contributions of the anode electrode to the electrode polarization.

Modeling of the electrode polarization was conducted by fitting the impedance spectra to an equivalent circuit comprising a resistor and two parallel resistance-capacitance (RC) circuits, shown in Figure 1(b). The inset table in Figure 2(b) shows that increasing the direct current density bias from 0.03 to 0.09 A/cm² increased the capacitance at low frequencies C_L from 0.0176 F/cm² to 3.979 F/cm². The increase in the anode capacitance of the equivalent circuit suggests accumulation of charges at the anode electrode. Results from these studies revealed that operation of the fuel cell in Ohio #5 coke at high current densities results in large anode overpotentials that can be ascribed to an increased capacitance of the Ni/YSZ anode. Development of a highly active anode catalyst would require tailoring the morphology and composition of the anode electrode, with the purpose of

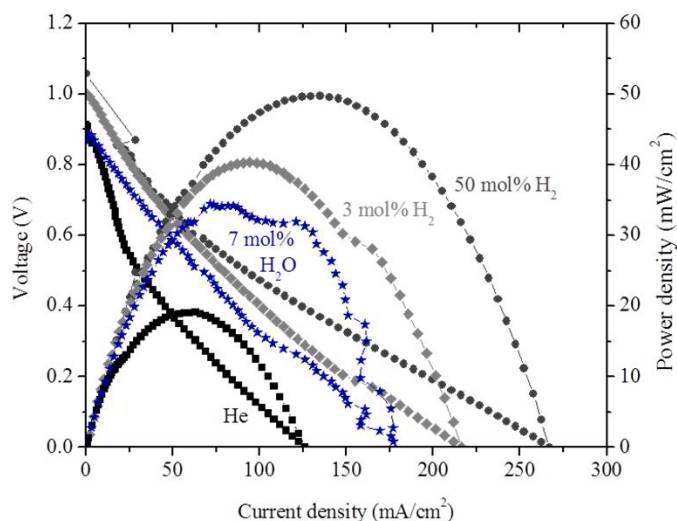


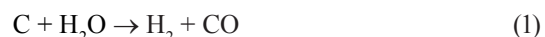
FIGURE 2. V-I curve of the fuel cell recorded at 800°C in 4 g of coconut carbon and H₂/He (100 sccm, 3 and 50 mol% H₂), He/H₂O (100 sccm, 17 mol% H₂O) and pure He (100 sccm)

reducing the accumulation of charges at the anode surface and improving the anode electronic conductivity.

Demonstrating the Operation of the Carbon SOFC with Addition of H₂O

Figure 2 shows V-I curves recorded from the carbon fuel cell operated in flowing H₂/He, He, and H₂O/He.

The fuel cell produced maximum power density as high as 50.4 mW/cm² in flowing 50 mol% H₂, and 19 mW/cm² in flowing He. Reducing the concentration of H₂ from 50 mol% to 3 mol% decrease the maximum power density to 40.0 mW/cm² indicating that the concentration of H₂ as low as 3 mol% can maintain the Ni particle in the anode structure in reduced state. Replacing the H₂-containing feed by H₂O/He (100 sccm, 7 mol% H₂O) produced a maximum power density of 34 mW/cm², 1.7 times higher than the power density obtained in pure He and only 15% lower than the performance in 3 mol% H₂/He. The relatively high fuel cell performance in H₂O/He feed could result from formation of H₂ at the anode electrode due to reactions involving carbon from coconut coke, and H₂O (reaction 1), and subsequent electrochemical oxidation of H₂ by O²⁻ diffused from the cathode electrode (reaction 2).



Integration of Individual Fuel Cells in Series and Parallel Stacks

Testing two fuel cells in series configuration using H₂ fuel produced an open-circuit voltage (OCV) of 2.0 V, closely resembling the expected Nernst potential in H₂ at 750°C, and a maximum current of 180 mA, as shown in Figure 3(a). Changing the gas feed from H₂/He to He allowed operating the stack in petcoke, producing an OCV of 1.2 V. The observed fuel cell OCV was found 30-35%

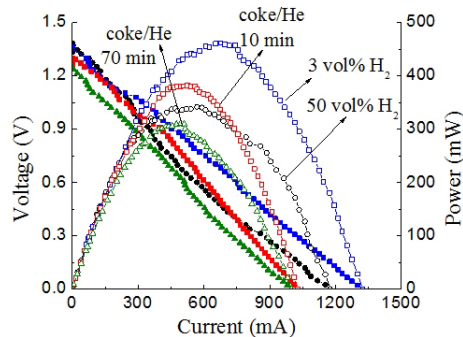
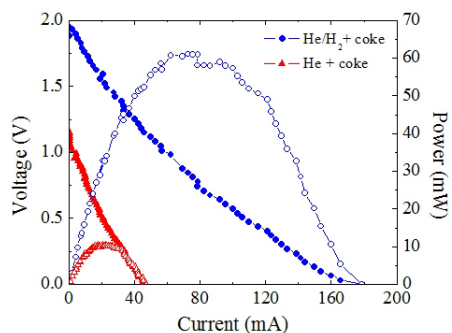
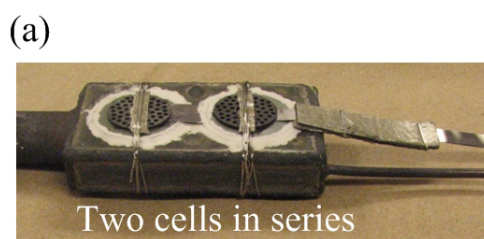


FIGURE 3. Effluent molar concentration profile during fuel cell testing at 800°C in 4 g of coconut carbon and H₂/He (100 sccm, 3 vol.% H₂), pure He (100 sccm), and H₂O/He (100 sccm, 17 mol% H₂O)

lower than the Nernst potential expected from two cells connected in series and operating in carbon fuel at 750°C. The lower performance of the fuel cell in petcoke reflects the limited contact area between the anode and the carbon fuel. Figure 3(b) shows a picture of a two fuel cell parallel stacks connected in series, designed with the purpose of producing (i) high current due to the parallel configuration of each fuel-cell-parallel-stack, and (ii) high voltage due to their integration in series. Testing of the stack in H₂ and coconut carbon produced an OCV of 1.3 V and maximum current of 1,200 mA. Replacing the gas feed from 50 to 3 vol% H₂ only decreased the fuel cell maximum current from 1,200 to 1,050 mA, indicating that electrochemical oxidation of coconut carbon has a significant contribution to the generation of electric current. Replacing the gas feed from 3 vol% H₂ to pure He did not cause major changes in the voltage and current characteristic of the fuel cell stack. The high performance of the two fuel cell parallel stacks reflects the advantages of the series and parallel configuration as well as the high reactivity of the coconut carbon.

Evaluating the Effect of Fuel Cell Load on the Formation of CO and CO₂ and the Fuel Cell Efficiency

The evolution of gases from direct utilization of carbon in SOFC was studied by potentiostatic/galvanostatic discharge of a fuel cell operated with coconut coke, a carbonaceous material with low ash and sulfur content. Operation of the carbon SOFC at 750°C produced less CO and more CO₂ than those predicted by thermodynamic calculation using total Gibbs-free energy minimization method. The addition of CO₂ to the anode chamber increased the CO formation and the maximum power density from 0.09 to 0.13 W/cm², indicating the occurrence of Boudouard reaction ($\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$) coupling with CO electrochemical oxidation on the fuel cell. Analysis of CO and CO₂ concentration as a function of current and voltage revealed that electricity was mainly produced from the electrochemical oxidation of carbon at low current density and produced from the electrochemical oxidation of CO at high current density. The results suggest the electrochemical oxidation of solid carbon has more mass transfer limitations than the electrochemical oxidation of CO.

Figure 4 shows the CO and CO₂ equilibrium molar flow rates as a function of temperature for the carbon SOFC with He feed at a current density of 0.50 and 1.0 A/cm². The equilibrium calculation indicates that elevating the SOFC operating temperature from 500 to 750°C increases the CO flow rate. At temperatures above 750°C, CO becomes the dominant product while CO₂ flow rates decrease to 0.01 μmol/s. As a result the operation of the carbon SOFC at lower temperatures can increase the CO₂/CO molar flow rate ratio. The operation at high current densities (i.e., 1 A/cm²) can also result in higher CO₂/CO ratio as shown in Figure 4(b), and as suggested by previous thermodynamic studies of carbon

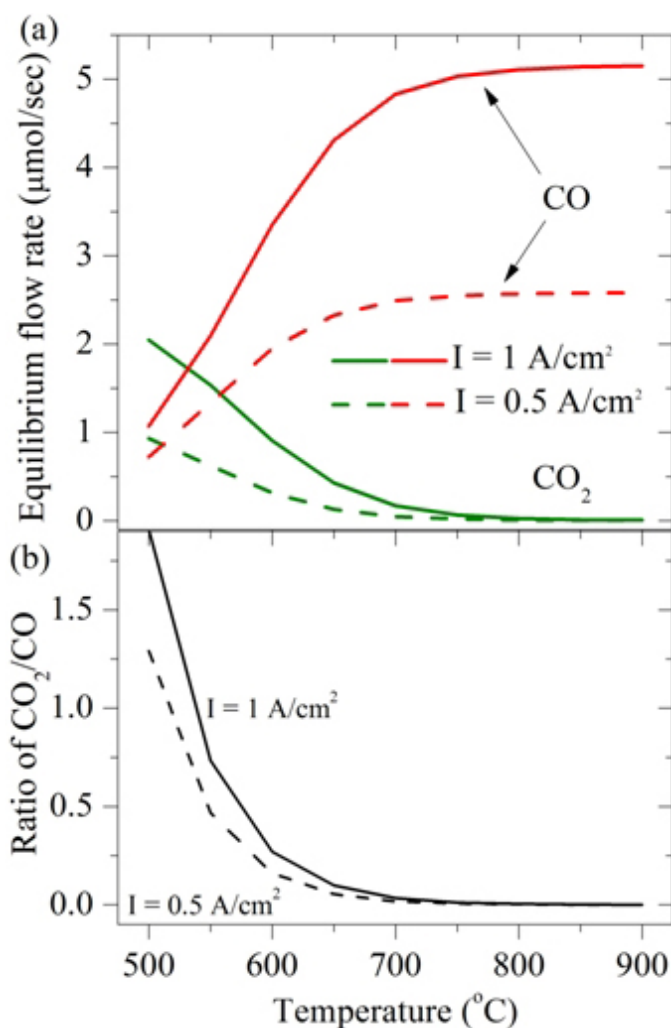


FIGURE 4. Plot of (a) CO and CO₂ equilibrium flow rates and (b) ratio of the equilibrium CO₂/CO flow rates as a function of temperature for the carbon SOFC operated at 0.5 and 1 A/cm² on carbon with He feed (200 sccm)

fuel cells [1]. Evolution of high CO₂/CO molar flow rate ratios benefits the carbon SOFC energy conversion efficiency, since electrochemical oxidation of carbon producing CO₂ is a four-electron process and that of CO is a two-electron process [2].

Table 1 summarizes the efficiencies of the carbon fuel cell under various fuels. The thermodynamic efficiency was calculated by relating the electric power produced by the fuel cell at the operating voltage (0.4 V) and the enthalpy change of the carbon oxidation reaction. The net efficiency represents the theoretical limiting efficiency of the fuel cell at 0.40 V and 750°C. The thermodynamic efficiency of fuel cell operating on carbon was higher than that of carbon with flowing of CO. This result indicates that the presence of CO in the anode compartment decreases the efficiency of the fuel cell, despite the improvement in energy generation. The decrease in thermodynamic efficiency in presence of CO is also in agreement with the decrease of net efficiency.

The efficiency of carbon fuel cell with flowing of CO was estimated to be between the net efficiency of the fuel cell operated with CO up to that operated with carbon.

TABLE 1. Summary of the Carbon Fuel Cell Efficiencies

Fuel	Thermodynamic Efficiency	Net Efficiency
Carbon	49.4%	52.8%
Carbon+CO	40.7%	33.1-52.8%
CO	N/A	33.1%

Conclusions and Future Directions

Studies conducted during FY 2012 documented that the anode charge separation majorly contributes to polarization loss, which limits the performance of the fuel cell. Demonstration of the improvement in the carbon fuel cell power generation with addition of H₂O, and evaluation of the efficiency of the carbon SOFC operated in coconut carbon were also reported.

Future studies will be focus:

- Investigation of the change in coal structure and properties resulting from coal pyrolysis process which will be integrated to the carbon fuel cell.
- Demonstration the long-term operation of the carbon fuel cell stack in series and parallel configuration.
- Evaluation the efficiency of the carbon fuel cell operation with coal and coke.

FY 2012 Publications/Presentations

1. Tritti Siengchum, Felipe Guzman, Steven S.C. Chuang, Analysis of Gas Products from Direct Utilization of Carbon in a Solid Oxide Fuel Cell. *Journal of Power Sources* **2012**, 213 (0), 375-381.

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2. S. Nurnberger, Bu, P. Desclaux, B. Franke, M. Rzepka, U. Stimming, Direct carbon conversion in a SOFC-system with a non-porous anode, *Energy & Environmental Science*, 3 (2010) 150-153.