V.O.3 Development of Kilowatt-Scale Coal-Based Fuel Cell Technology*

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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 megawatt-scale coal-based SOFC technology. Objectives for 2010 included the following:

- Determine the effect of CO and CO_2 on the performance of the coal-based fuel cell.
- Study the long-term electrochemical oxidation of coke.
- Investigate the integration of fuel cells in series and parallel for the coal fuel cell stack.
- Evaluate the operation conditions of a steel coal injection unit.

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

(D) System Thermal Management

Technical Targets

This project is directed at the development of kilowatt-scale coal-based SOFC technology. This project will develop a technological basis for the scale up of power generation capability of a kW SOFC to megawatt scale. A current density of 100 mA/cm^2 at 0.4 V was the initial target for demonstration of a coal-based SOFC.

Accomplishments

Year 2010 focused on the following milestones:

- Studied the effect of CO and CO_2 on the activity of the anode catalyst and the performance of the coal-based fuel cell. Exposure of the Ni anode to CO was found to improve the fuel cell performance and decrease the fuel cell energy efficiency.
- Investigated the integration of fuel cells in series and parallel for the coal-based fuel cell stack. Integration of fuel cells in parallel was found to produce maximum current densities 30% higher than integration in series.
- Demonstrated the long-term electrochemical oxidation of coke.

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Introduction

The direct use of coal in the SOFC to generate electricity is an innovative concept for electric power generation. The coal-based fuel cell could offer significant advantages: (i) minimization of NO_x emission due to its operating temperature range of 700-1,000°C, (ii) high overall efficiency because of the direct conversion of coal to CO_2, (iii) the production of a nearly pure CO_2 exhaust stream for the direct CO_2 sequestration, and (iv) low investment and maintenance cost due to simplicity of the process. This technology also promises to provide low cost electricity by expanding utilization of U.S. coal supplies and relieving our dependence on foreign oil.

A small-scale coal fuel cell 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 fuel cell fabrication techniques, and (iii) testing a small-scale coal fuel cell 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

Anode supported fuel cells were fabricated by the tape casting and screen printing approach, which involves: (i) generating a Ni-yttria-stabilized zirconia (YSZ) anode support layer (70 wt% Ni), a Ni-YSZ interlayer (50 wt% Ni), and a high purity YSZ electrolyte layer, (ii) cutting the layers in the shape of a 2 cm diameter disc and co-firing at 1,400°C, and (iii) screen printing and firing at 1,200°C a lanthanum strontium manganese (LSM)-YSZ cathode layer. The cells were tested in a steel reactor comprising a gas inlet port, a coke feeding mechanism, and a gas exhaust outlet port connected to a mass spectrometer (Pfeiffer Omnistar) and a gas chromatographer (SRI 8610 C). Ag paste was coated along the perimeter of the anode electrode to enhance the contact between the anode and the steel reactor serving as anode current collector; Ag mesh and Ag paste current collectors were attached to the cathode electrode. The fuel cell performance and energy efficiency was evaluated by introducing the fuel (H_2, coke and coal) and monitoring the current produced at different voltage loads.

The microstructure of the fuel cell electrodes was characterized before and after the testing experiments by X-ray fluorescence, scanning electrode microscopy, and energy dispersive X-ray spectroscopy, with the purpose of monitoring the reducibility of the fuel cells fabricated in-house. The performance and energy efficiency of the fuel cell was tested in coke, a carbonaceous fuel produced by the pyrolytic reaction of coal at high temperature (800-950 °C). The effect of CO_2 product on the anode catalyst activity and performance was investigated. Fuel cell efficiencies were calculated by considering the power produced by the cell and the heat of combustion of the fuel consumed during the electrochemical reaction. Once sufficient understanding was gained for (i) the reaction mechanism of electrochemical oxidation of coal-based fuel on the anode electrode, (ii) the effect of CO_2 on the performance of the fuel cell, (iii) the microstructure of the anode electrode (porosity, tortuosity, and stability), and (iv) the coal feeding approach, efforts were expanded to the development of new anode catalysts, fuel cell fabrication methods, and current collection assemblies for stack fabrication.

Results

The effect of CO on the performance of the fuel cell was studied by testing of the cell in coke and different concentrations of CO, monitoring the power produced

and the composition of the gases at the fuel cell exhaust. Figure 1(a) shows testing of the fuel cell in 3.0 g of coke and He (200 sccm) under open circuit voltage (OCV) conditions and at a load of 0.4 V produced a maximum current of 190 mA, and the formation of CO and CO_2 product. The concentration of the CO and CO_2 products were determined from the mass spectrometer profiles and gas chromatograph analysis of the exhaust stream. The thermodynamic efficiency (ε_T) of the fuel cell during operation in coke was determined to be 49.4% from the data of Figure 1(b), by relating the electric power produced by the fuel cell at the operating voltage, W_e, and the enthalpy change of the carbon oxidation reaction, ΔH. W_e was estimated from Figure 1(b) by integrating the highlighted area under the current vs time curve. The enthalpy change of reaction, ΔH, was estimated considering the amount of carbon consumed during the electrochemical oxidation reaction and the low heating value of coke. The amount of coke consumed was determined by combination of the increase of CO and CO_2 concentration in the outlet stream when changing the operating conditions from OCV to 0.40 V, as summarized below

$$\varepsilon_T = \frac{W_e}{\Delta H} = \frac{V \int I \, dt}{LHV \cdot ([CO + CO_2]_{0.40V} - [CO + CO_2]_{OCV}) \cdot F_{outlet} \cdot U \cdot t}$$

$$\varepsilon_T = \frac{0.4 \cdot 144.75}{355,200 \cdot 0.0165 \cdot 10^{-3} \cdot 1 \cdot 20} = 49.4\%$$

LHV=lower heating value of carbon (J/mol)

$([CO + CO_2]_{0.40V} - [CO + CO_2]_{OCV})$ = increase in the concentration of CO and CO_2(mol/ml)
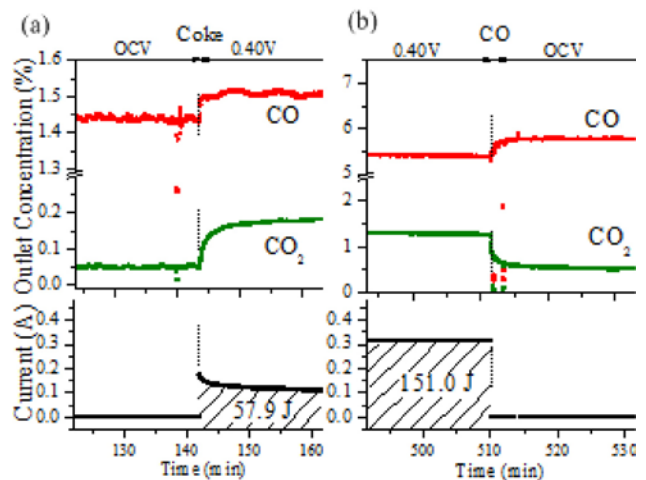
U=fuel utilization (%)

t=time (sec)

FIGURE 1. CO and CO_2 concentration at the exhaust of the fuel cell and current produced at 800°C, OCV, and 0.4 V during testing in (a) coke (3g) and He (200 sccm), and (b) coke (3g) and He containing 6.97% CO.

Figure 1(b) shows testing of the fuel cell in coke and a He stream (200 sccm) containing 6.97% CO at OCV and 0.4 V produced a higher current than that observed with coke, reaching values close to 320 mA. The efficiency of the fuel cell during testing in coke and CO, determined from the data in Figure 1(b), was found to be lower than that of the fuel cell in coke despite producing a higher current. The efficiency of the fuel cell in coke and CO was calculated by relating the electric power produced by the fuel cell at the operating voltage, W_e, and the enthalpy change of the carbon oxidation reaction, ΔH. The enthalpy change of reaction, ΔH, was estimated considering the amount of CO consumed during the electrochemical oxidation reaction and the low heating value of CO. The amount of CO consumed was determined by the difference in CO_2 concentration in the outlet stream when switching the operation from 0.40 V to OCV.

$$\varepsilon_t = \frac{W_e}{\Delta H} = \frac{V \int I \, dt}{LHV \cdot ([CO_2]_{0.4V} - [CO_2]_{OCV}) \cdot F_{outlet} \cdot U \cdot t} = \frac{0.4 \cdot 377.50}{282.900 \cdot 0.066 \cdot 10^{-1} \cdot 1 \cdot 20} = 40.7\%$$

LHV=lower heating value of carbon (J/mol)

$([CO_2]_{0.4V} - [CO_2]_{OCV})$ = increase in the CO_2 concentration of (mol/ml)

U=fuel utilization (%)

t=time (sec)

The reproducibility of these results was further investigated, quantifying the concentration of gas species at the exhaust, as summarized in Tables 1 and 2.

TABLE 1. Fuel Cell Efficiency and Composition of Gases at the Fuel Cell Exhaust

Setting		Inlet (%)		Outlet (%)			
V (V)	Inlet gas	CO	He	O_2	N_2	CO	CO_2
OCV	He	0	100	0	0.01	1.43	0.05
0.4	He	0	100	0	0.01	1.51	0.18
0.4	He/CO	6.97	93.03	0	0.007	5.38	1.28
OCV	He/CO	6.97	93.03	0	0.007	5.77	0.51

TABLE 2. Fuel Cell Efficiency in Coke and CO

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

Figure 2 shows a schematic representation of the approach used for integrating two fuel cells in series and in parallel, and their corresponding fuel cell voltage and current characteristics (i.e., fuel cell voltage-current curves) during testing in H_2 fuel. The experimental

apparatus was intentionally constructed to allow measuring the individual performance of each cell. Inspection of Figure 2 shows integration of the fuel cells series produced a maximum current of 1.8 A, which corresponds to nearly 95% of the sum of each individual cell maximum current; the current expected from the two cells connected in a series arrangement. The maximum power output produced by the cells in series arrangement was found to be 0.35 W, as evidenced from the curves in Figure 2.

Testing of the cells in a parallel arrangement produced a fuel cell current close to that of the individual cells, with a maximum power output of
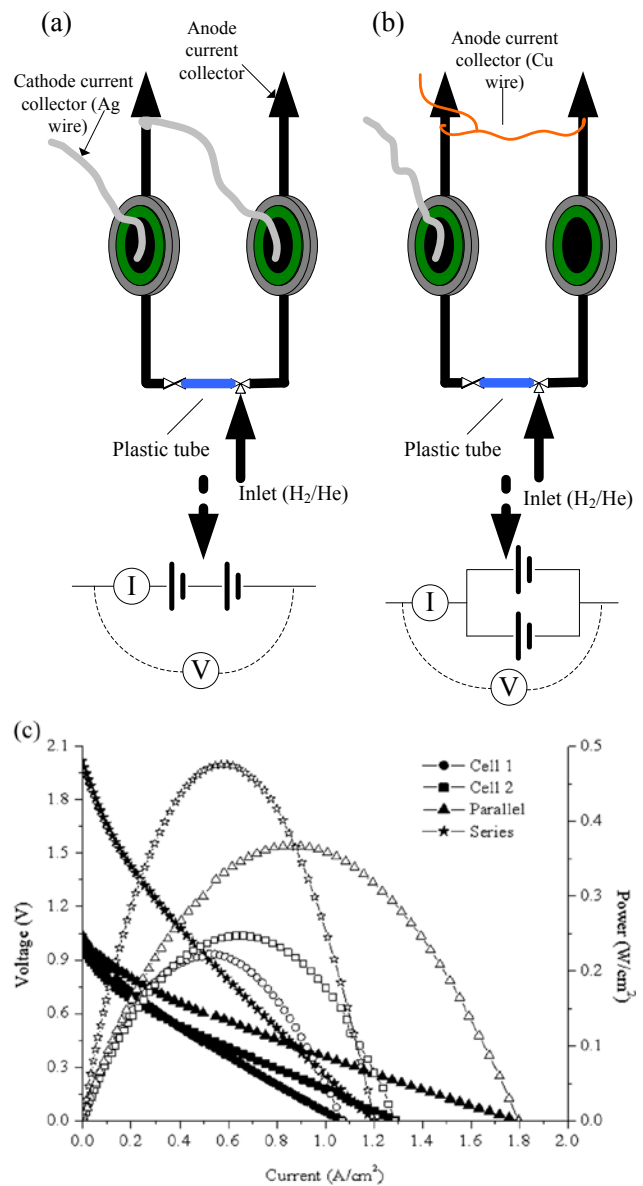
FIGURE 2. Schematic of fuel cells set up (a) in series, (b) in parallel, and (c) voltage-current curve of individual cell, series set-up and parallel set-up.

0.495 W, 30% higher than observed for the cells in the series configuration.

The higher power outputs observed with parallel configuration was further investigated by testing a system composed of four small cells (1 cm diameter) in H_2 fuel, as shown in Figure 3. Testing of the cells in the parallel configuration demonstrated the buildup of power output needed for the coal fuel cell stack. Future experiments will evaluate the performance characteristics of the fuel cell stack configuration during operation in coal and coke fuel. The efficiency of the coal fuel cell stack in the parallel configuration will be analyzed in future work.
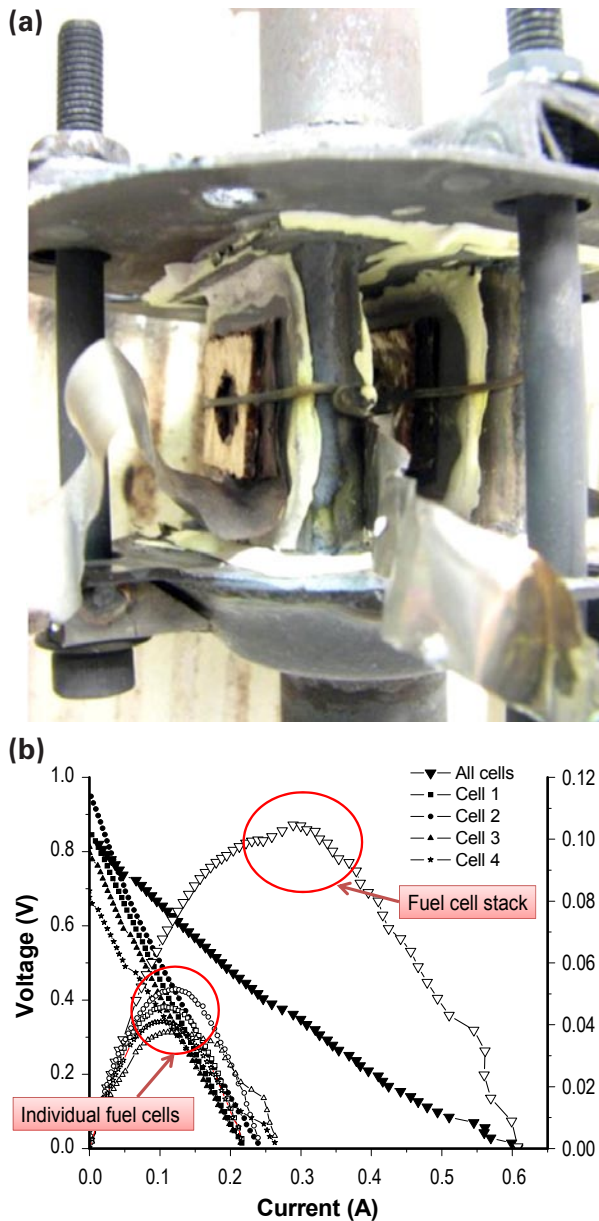
Figure 4 shows the current density as function of time during testing of a fuel cell in coke fuel and He flow at 800 C and a load of 0.35 V. Exposure of the fuel cell to H_2 CO and CO_2 after 15 h of continuous operation resulted in rapid increases in the fuel cell current density. The increases of the fuel cell current density can be explained by the combined electrochemical oxidation of H_2 and coke, and CO and coke. The increase in the fuel cell current density during exposure to CO_2 evidenced the electrochemical oxidation of coke produced by the reaction of carbon and CO_2 ($C+CO_2 \rightarrow 2CO$). The effect of CO_2 on the performance of the fuel cell will be further investigated in future experiments.

Conclusions and Future Directions

- Exposure of the Ni anode to CO was demonstrated to improve the fuel cell performance and decrease the fuel cell energy efficiency.
- Integration of fuel cells parallel configuration was found to produce maximum power outputs exceeding those of similar cells integrated in a series configuration by 30%.
- Long-term testing of the fuel cell in coke was demonstrated.

The proposed future research would be focused in the following directions:

- Identification of catalyst composition for long-term electrochemical oxidation of solid carbon fuels at 800°C
- Evaluation of the energy efficiency of fuel cell stacks in the series and parallel configuration.
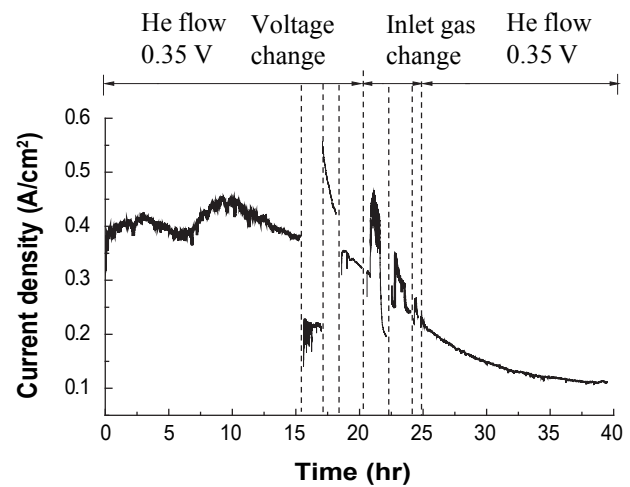
(a)

(b)

FIGURE 3. (a) A digital image of 4-cell fuel cell stack, (b) voltage-current curve of the individual cells and the fuel cell stack.

FIGURE 4. Current density of a fuel cell during testing in coke at 800°C and a load of 0.35 V. Note: 1. Voltage changed from 0.35 to 0.5, 0.1, and 0.35 volt, respectively, the inlet gas changed from He to He/H_2, He/CO_2, He/CO respectively, while the voltage was kept at 0.35 volt.

- Completion of design of the fuel cell stack and testing of a small-scale (1-10 kW) coal fuel cell system.
- Fulfill reporting obligations and preparing manuscripts for publications and conference presentations.

FY 2010 Publications/Presentations

1. "Performance and byproduct analysis of coal gas solid oxide fuel cell", Rahul Singh, Felipe Guzman, Rajesh Khatri, and Steven S.C Chuang; Energy & Fuels, (2010), 24 (2) p 1176.