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Contaminant Effects in Solid Oxide Fuel Cells

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CONTRACT INFORMATION

Contract Number DE-AC21-89MC26355

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Period of Performance February 1991 to June 1992

Schedule and Milestones

Program Schedule

	1991					1992				
	F	M	A	M	J	J	A	S	O	N
Test Plan	—									—
Fabrication		—	—	—	—					—
Testing			—	—	—	—	—	—	—	—
Analysis						—	—	—	—	—

OBJECTIVES

One objective of this study is to conduct a program to identify the long-term tolerance of the tubular solid oxide fuel cell (SOFC) to coal-derived fuel gas containing a mixture of three impurities: hydrogen sulfide (H_2S), hydrogen chloride (HCl), and ammonia (NH_3), with the

SOFC operating at 350 mA/cm^2 . Another objective is to learn whether the performance at 350 mA/cm^2 , of the SOFC would be affected by contact with silica (SiO_2), carried over as a hydrate. Post-test analyses are carried out to describe any interaction with the SOFC in terms of direct structural or chemical changes.

BACKGROUND INFORMATION

These tests, which provide a basis for estimating the effects of operating the SOFC in the presence of specific amounts of the coal gas impurities NH_3 , HCl , H_2S , and Si , significantly relate to the Fossil Energy Program by:

- Providing information and guidance toward SOFC materials and designs that adapt best to coal gas impurities.
- Contributing to the development of an efficient and environmentally acceptable SOFC power generation system by establishing coal gas clean-up criteria for system engineering.

PROJECT DESCRIPTION

Full-scale present-technology SOFCs are operated at 1000°C and 350 mA/cm^2 , to demonstrate performance in fuel gas containing various coal-derived impurities. This report details testing of the effect of three impurities in combination: NH_3 , HCl , and H_2S ; and also the effect of the single impurity Si . The following Table 1 fuel comprises a simulated coal gas composition representing the product obtainable from a Texaco Entrained-Bed oxygen-blown coal gasifier at 776°F after external desulfurization.

Table 1. Simulated O_2 -Blown Coal Gas

Gas	Mole %
CO	37.2
H_2	34.1
CH_4	0.3
CO_2	14.4
H_2O	13.2
N_2	0.8

This fuel continues to be employed in long-term life testing of the three combined impurities. It is also used in the initial tests evaluating Si as a fuel impurity. In other increasingly severe tests involving the single impurity, Si , the carryover of Si is enhanced by employing simulated partially reformed natural gas with progressively higher initial H_2O concentrations as shown in Table 2.

Table 2. Simulated Natural Gas (Partially Reformed) Mole Fraction

Gas	Mole %	
	Comp. A	Comp. B
CO	15.7	28.4
H_2	36.2	--
CH_4	3.3	11.6
CO_2	18.6	2.9
H_2O	26.2	56.7

Upon completion of testing, cells are examined in detail for evidence of physical or chemical damage. Experimental specifics of electrical testing and the theoretical basis of data interpretation are given in the Proceedings of the Third Annual Fuel Cells Contractors Meeting, pp. 109, 110.

RESULTS

Extended SOFC Testing at 1000°C Using Coal-Derived Fuel Gas With NH_3 , HCl , and H_2S Impurities

Two full scale (50-cm length) SOFCs, each representative of generator cells in the field, were electrically connected in series; then operated at 1000°C and 350 mA/cm^2 . An initial run of approximately 150 hours served to establish base-line performance in 89% H_2 , 11% H_2O fuel at 85% fuel utilization and 4 stoichs, air (Figure 1).

Figure 1. SOFC performance at 1000°C and 350 mA/cm², 85% fuel utilization and 25% air utilization. Fuel = simulated air-blown coal gas containing 5000 ppm NH₃, 1 ppm HCl and 1 ppm H₂S.

Then, for approximately 200 hours, a similar base-line was established for operation in simulated coal gas fuel (Table 1). Finally, the fuel impurity components were sequentially added, as indicated in Figure 1. The cumulative effect on performance as shown in Table 3.

These data reveal no strong association of cell resistance with cell performance change in the cases of NH₃ and HCl. When H₂S is added, resistance increases account for a minor part of the 0.06V decline observed for each cell over the first 24 hours. However, cell resistances thereafter change linearly, along with linearly declining voltages. In this latter phase, resistance accounts for a major part of each observed cell voltage decline.

SOFC Testing at 1025°C Using Coal-Derived Fuel Gas With NH₃, HCl, and H₂S Impurities

The same two SOFCs were subsequently continued in operation, but at a moderately higher temperature, 1025°C. As Figure 2 demonstrates, #1 cell tended to decline more slowly, and #2 cell continued to decline at the same rate as before, when it was operating at 1000°C. Later operation, without impurities, at 1025°C for 450 hours served to improve performance and stabilize the cells. When operation at 1000°C resumed, the cell resistance trend lines returned to approximately the original R vs. t slopes observed during 0-500 hours on test, signifying cessation of impurity-related voltage degradation.

Table 3. Effect of Three Impurities on SOFC Operation at 1000°C and 350 mA/cm² (From Figure 1)

Impurity Species	Order of Addition	ppm	Initial (24 hour) Voltage Drop (V)		Long-Term V vs. t Trend Line ($\Delta V/1000$ hrs)		ΔV Due to Cell Resistance Index Change ($\Delta V/1000$ hrs)	
			Cell #1	Cell #2	Cell #1	Cell #2	Cell #1	Cell #2
None	-	-	-	-	+0.01	+0.01	-0.01	-0.003
NH ₃	1	5000	0	0	+0.01	+0.01	-0.01	-0.003
HCl	2	1	0	0	-0.02	0.00	-0.01	-0.003
H ₂ S	3	1	.06	.06	-0.04	-0.04	-0.04	-0.025

Figure 2. SOFC performance at 1025°C and 350 mA/cm², 85% fuel utilization and 25% air utilization. Fuel = simulated air-blown coal gas containing 5000 ppm NH₃, 1 ppm HCl and 1 ppm H₂S.

Follow-On Long Term SOFC Testing at 1000°C

A new two-cell test was initiated; this time employing NH_3 at 5000 ppm, HCl at 1 ppm, but with H_2S reduced to 0.1 ppm. After approximately 500 hours on test, this lower level of H_2S demonstrates no measurable voltage degradation (Figure 3). Extension of testing at this level of impurities to approximately 3000-4000 hours is expected to show continued stable performance levels.

Overall Performance Loss

Similar cells are presently demonstrating lifetime capabilities up to 30,000 hours in the absence of impurities.

A good estimate of degradation, in these tests, attributable to impurity exposure is given by examination of the resistance trend lines. Experience shows that these trends lines tend to remain relatively constant over periods of time typified by this experiment. Four important observations can be made with regard to performance loss:

Figure 3. SOFC performance at 1000°C and 350 mA/cm², 85% fuel utilization and 25% air utilization. Fuel = simulated air-blown coal gas containing 5000 ppm NH_3 , 1 ppm HCl and 0.1 ppm H_2S .

- H_2S is responsible for most voltage losses experienced by this particular cell design.
- Voltage losses due to irrecoverable resistance increases are: cell #1 - 0.021V; cell #2 - 0.025V, or $\leq 1\%/1000$ hrs.
- In the presence of impurities, cell resistances increase at a lower rate at 1025°C , compared with 1000°C .
- When impurities are removed, cell resistance trends return to the lower rates of increase shown at the beginning of cell operation.

Short-Term SOFC Testing at 1000°C and 350 mA/cm^2 Using Coal-Derived Fuel Gas With Silicon Impurity

Two full-scale (50 cm length) SOFCs show near-normal performance after approximately 2400 hours exposure to simulated coal gas contaminated with silicon by permeation through a fixture held at $900\text{--}1000^\circ\text{C}$; composed of "Duraboard", a porous material composed of 74% Al_2O_3 and 26% SiO_2 . Some accumulation of silicon observed on exposed nickel in the fuel electrode (Figure 4) was insufficient to cause appreciable degradation. As a follow-up, experiments to increase silicon carryover are in progress to induce more silicon accumulation on the fuel electrode, and more significant degradation. Silicon detected is assumed to be present as silica, SiO_2 .

Short-Term SOFC Testing at 1000°C Using and 350 mA/cm^2 Simulated Partially Reformed Natural Gas

A follow-on test employing partially reformed natural gas offers the ability to investigate the effect of increasing H_2O levels on silicon transport. This test differs from the prior run with

respect to the composition of the "Duraboard" through which the fuel must permeate. Compared to approximately 13.2% H_2O in the simulated coal gas, these experiments employ successively higher H_2O concentrations as described in Table 2.

The effect of silicon on SOFC operation at 1000°C , 350 mA/cm , 4 stoichs, air, and 85% fuel utilization is shown in Figure 5. On H_2 fuel, the cells can be seen to improve in performance over approximately 600 hours. Then, when continued on with composition "A" fuel (26.2% H_2O) performance still increases slightly, with a possible tendency to stabilize. Also, the resistance index of both cells changes from a stable level to a slightly positive slope, consistent with the expectation of faster delivery of silicon contamination to the test cells.

Upon changing to fuel gas composition "B", with 56.7% H_2O , the loaded voltage of each cell shows a stable-to-declining characteristic. Concurrently, the trend lines for each cell resistance index begin a new and higher positive slope equivalent to a voltage degradation (ΔV) of 0.008 to 0.012V per 1000 hours. Ultimately, silicon accumulation may fully counterbalance the natural tendency of these cells to improve; then the effect of increasing cell resistance is expected to be seen in a negative slope for loaded voltage vs. time.

Silicon Carryover as a Fuel Contaminant

Silica transport may occur when the H_2O content in the fuel contacts the silica present in the Duraboard fixture through which the fuel must flow:

Backscattered electrons
Arrows indicate silicon-rich areas

Silicon element map of area shown above

Figure 4. Location of silicon-rich areas at exposed nickel network of SOFC fuel electrode, after approximately 2,400 hours of operation at 1000°C in simulated coal gas (13% H₂O) with Si impurity.

Figure 5. SOFC performance at 1000°C and 350 mA/cm², 85% fuel utilization and 25% air utilization. Fuel Containing 1) 11% H₂O, 2) 26.2% H₂O, (Fuel A), 3) 56.7% H₂O (Fuel B) passing over silica, SiO₂.

As the CH₄ component in the fuel reforms to CO and H₂, water is consumed:

which favors reversal of reaction (1):

causing silica, SiO₂(s) to deposit farther downstream; possibly on the SOFC fuel electrode, causing accumulating on exposed nickel surfaces (Figure 4).

Coverage of nickel by silica would impede transport of H₂ fuel and increase electrical resistance. Most of the observed increase in electrical resistance is attributable to this effect.

Pore blockage has not yet been observed, but if it does, it will be measurable by an increase in slow polarization due to the counter diffusion of H₂O and fuel.

The major accomplishments of this work can be summarized in the following conclusions:

- 1) Ammonia impurity up to 5000 ppm in simulated coal gas does not present a measurable contribution to SOFC voltage degradation over approximately 2500 hours of testing. As testing time increases, NH₃ contaminant effects are expected to be nil.
- 2) HCl impurity at 1 ppm in simulated coal gas does not have a detectable effect on SOFC performance up to 2,200 hours under the stated test conditions.

- 3) H_2S impurity at 0.1 ppm in simulated coal gas fuel can be tolerated by state-of-the-art SOFCs, along with 5000 ppm NH_3 and 1 ppm HCl with no measurable voltage degradation over at least 500 hours.
- 4) Silicon impurity in coal gas can be carried over to the SOFC and deposited. The carryover is enhanced by high H_2O content (~50%) in the fuel. Under conditions expected for oxygen-blown coal gas fuel ($\text{H}_2\text{O} = 13\%$) silicon is not expected to have a major effect on SOFC performance.

FUTURE WORK

Continue a program to identify the long-term tolerance of the SOFC to simulated coal gas containing a mixture of the three impurities: NH_3 , 5000 ppm, HCl , 1 ppm, and H_2S , 0.1 ppm.

Complete short-term tests of the effect of Si in SOFC fuel gas, describing the results of enhanced carryover due to high-steam content in the fuel.

Initiate testing of SOFCs with modified fuel electrode materials or processes that may increase the sulfur tolerance.

Initiate testing to identify short-term tolerance of the SOFC to selected other individual coal gas impurities. These contaminants, including zinc (Zn), iron (Fe), aluminum (Al), potassium (K), and calcium (Ca) will all be eventually included in a multi-impurity long-term test along with NH_3 , HCl , and H_2S .

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