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HIGH-TEMPERATURE, SOLID OXIDE ELECTROLYTE FUEL
CELL POWER GENERATING SYSTEM

Annual Report for the Period June 1, 1980—May 31, 1981

MASTER

October 14, 1981

Work Performed Under Contract No. AC02-80ET17089

Westinghouse Electric Corporation
Pittsburgh, Pennsylvania

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HIGH-TEMPERATURE, SOLID OXIDE ELECTROLYTE
FUEL CELL POWER GENERATING SYSTEM

Annual Report
Covering the Period
June 1, 1980 to May 31, 1981

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Research and Development Center
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October 14, 1981

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TABLE OF CONTENTS

	<u>Page(s)</u>
1.0 Preface	1
2.0 Abstract	2
3.0 Conclusions	3
4.0 Present Program	5
5.0 Overall Technical Effort	6
5.1 Technology Development	6
5.1.1 Porous Support Tube Refinement	6
5.1.1.1 Support Tube Fabrication	7
5.1.1.2 Support Tube Experiments	8
5.1.1.3 Support Tube Gas Transport Properties	15
5.1.2 Air Electrode Development	21
5.1.2.1 Thermal Expansion of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$	23
5.1.2.2 Electrical Conductivity of Lanthanum Manganites	23
5.1.2.3 Oxygen Loss from $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$	28
5.2 Fuel Cell Stack Advancement	34
5.2.1 Bench Testing of Stacks Under Simulated Service Conditions	34
5.2.1.1 Sulfur Tolerance of Stack #8	35
5.2.1.2 Sulfur Adsorption of Nickel	37
5.2.1.3 Sulfur Impurity-Thermodynamic Considerations	41
5.2.1.4 Bench Testing of Cells	46
5.2.1.4.1 Tests of Multi-Cell Stacks #11, 13, 14, 15, 16, 17, 18	46
5.2.1.4.2 Bench Testing of FBA-Type Cells	56
5.2.1.5 Diagnostic Fuel Cell Testing at Reduced Temperatures	61
5.2.1.5.1 Facilities for DC and AC Bench Testing of Stacks	65
5.2.1.5.2 Verification Tests for AC Measurement System	66

TABLE OF CONTENTS (Cont.)

	<u>Page(s)</u>
5.2.1.5.3 Analytical Bench Testing of Stacks ...	73
5.2.1.5.4 Computer Simulation of FBA Cell Behavior	80
5.2.1.5.5 Dielectric Characteristics of an FBA Cell near Room Temperature	83
5.2.1.5.6 Analyses of AC Data on FBA Cell #3 ...	86
5.2.1.5.7 Analyses of DC Data on FBA Cell #3 ...	88
5.2.1.5.8 Analyses of Current Distribution in the IC and Electrolyte Layers	88
6.0 Future Work	94
7.0 References	96
8.0 Appendix A	97

LIST OF FIGURES

<u>Figure</u>	<u>Title</u>	<u>Page</u>
5.1	Support Tube Extrusion Die	9
5.2	Assembled Support Tube Extrusion Die	10
5.3	Tensile Strength of Porous Support Tubes	12
5.4	Samples of Open and Closed-End Tubes	14
5.5	Schematic of Apparatus for Measuring Gas Interdiffusion Coefficient and Gas Permeation Coefficient of Porous Support Tube	16
5.6	Schematic of Apparatus for Measurement of Partial Permeation Coefficient and the Distribution of Pore Sizes	19
5.7	Thermal Expansion of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$	24
5.8	Thermal Expansion of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$	25
5.9	Thermal Expansion of $\text{La}_{.7}\text{Ca}_{.3}\text{MnO}_3$ Showing Phase Transformation	26
5.10	Resistivity of Pure and Substituted Lanthanum Manganite	27
5.11	Fraction, x, Substitution for $\text{La}_{1-x}\text{M}_x\text{MnO}_3$	29
5.12	Oxygen Loss From $\text{La}_{.5}\text{Ca}_{.5}\text{MnO}_{3-x}$ versus O_2 Partial Pressure	30
5.13	Change of Equilibrium Constant with Oxygen Partial Pressure for Interaction of Oxygen with $\text{La}_{.5}\text{Ca}_{.5}\text{MnO}_{3-x}$	32
5.14	Sulfur Tolerance Test on Stack No. 8	36
5.15	Adsorption at 1000°C at Sulfur-containing Gas Species on a Nickel Powder Bar	38
5.16	Rate of Sulfidation and Desulfidation at 1000°C of a Sintered Nickel Powder Bar	40
5.17	Tolerance of Nickel to Sulfidation in $\text{H}_2/\text{H}_2\text{O}/\text{N}_2$ Atmosphere at 1000°C	42

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Title</u>	<u>Page</u>
5.18	Minimum Tolerance of Nickel Electrodes to Sulfidation as a Function of Fuel Gas Composition	43
5.19	Voltage at which Minimum Tolerance to Sulfidation Occurs as a Function of Fuel Composition and Temperature	44
5.20	Performance of Cell Stack #11, Having Variable Length Cells	47
5.21	Performance of Cell Stack #13	49
5.22	Performance of Cell Stack #13 as a Function of Time at Temperature (1000°C)	51
5.23	Performance of Cell Stack #14	52
5.24	Performance of Cell Stack #15	54
5.25	Performance Characteristics of Cell Stacks #16, 17, 18	53
5.26	Performance of First FBA Fuel Cell	57
5.27	Air Electrode Half Cell Tests	59
5.28	Open Circuit Potential versus Temperature for FBA Cell #3	62
5.29	Effective Cell Resistance Under Load versus Temperature for FBA Cell #3	64
5.30	Typical Schematic Diagram for DC Stack Measurements ...	67
5.31	Typical Schematic Diagram for AC Stack Measurements ...	68
5.32	Schematic Diagram for Stack Gas Supply System	69
5.33	Simulated Power Sources Within (A) Purely Resistive Internal Impedance or (B) Frequency Dependent Internal Impedance	70
5.34	Verification Tests of AC Measurement System	72
5.35	DC Current-Voltage Characteristic for 9 Cells of Stack #9; Operating on Lean Fuel and Air	74
5.36	The Differential Resistance ($\Delta V/\Delta I$) versus Current (I) for Stack #9, Operating on Lean Fuel and Air	75

LIST OF FIGURES (continued)

<u>Figure</u>	<u>Title</u>	<u>Page</u>
5.37	Complex Impedance Data, Experimental and Calculated, for Fuel Cell Stack #9	77
5.38	Equivalent Circuit for the Intermediate and High Frequency Polarizations of Stack #9	78
5.39	Current-Voltage Characteristic of an FBA Cell, as Predicted by Computer Simulation	81
5.40	Current Density in an FBA Cell as a Function of Position Along the Cell, as Predicted by Computer Simulation	82
5.41	Dielectric Parameters versus Frequency for FBA Cell #3 at 44°C	84
5.42	Complex Impedance for FBA Cell #3, Operating at 800°C on Lean Fuel and Air	87
5.43	DC Current Voltage Characteristic for FBA Cell #3, Operating at 800°C on Lean Fuel and Air	89
5.44	Differential Polarization Ratio versus Current for FBA Cell #3, Operating at 800°C on Lean Fuel and Air	90
5.45	Schematic of an Air Electrode-Interconnection-Fuel Electrode System (A) and the Finite Element Analog to the System (B)	92
5.46	Relative Current Density versus Position Along the Interconnection for the System Shown in Figure 5.45	93

LIST OF TABLES

<u>Table</u>	<u>Title</u>	<u>Page</u>
5.1	Tensile Strength of Porous Support Tubes	11
5.2	Thermal Expansion Data Obtained on Various Candidate Air Electrode Materials	22

1.0 PREFACE

This program is technically managed at Argonne National Laboratories/DOE, under Dr. J. P. Ackerman, with Dr. A. V. Fraioli, as his Deputy Assistant Manager. It is contractually managed by Mr. R. J. Gariboldi of the DOE Chicago Operations Office. Mr. M. Zlotnick, and G. W. Tittmore, of the Department of Energy, are responsible for the overall administration of the program. Their assistance and guidance in program planning, program interaction and in direct contract-related matters is gratefully acknowledged.

2.0 ABSTRACT

Closed-end tubes are now being prepared in-house, for use in fabricating and evaluating the FBA cell design. New perovskite-type mixed oxides are being investigated as air electrode materials and some have been identified and are being used in FBA cell test evaluation studies. Initial FBA cells have been fabricated and tested. Although their performance is below target goals, fabrication procedures for all fuel cell components have been verified for cell construction. Areas of investigation for FBA cell performance improvement have been identified and work is proceeding in these areas. Variable-length cells in the series-cell stack design have demonstrated high (85%) fuel utilization with good performance ($0.57\bar{V}$ at 400 mA/cm^2 average, simulated coal derived fuel, 1000°C).

3.0 CONCLUSIONS

1. Closed-end support tubes are now being fabricated for the FBA design cell.
2. Air electrode development has identified doped perovskites of the type $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ as promising alternatives to tin-doped indium oxide. These compositions are useful in constructing the FBA-type cell.
3. Studies have indicated that air electrode polarization, due to oxygen loss from the air electrode material, will be minimal, as long as the electrode is sufficiently porous.
4. Sulfur tolerance studies, conducted on series-cells stacks, indicate no harmful or permanent effects on performance at a level of 50 ppm H_2S in a 85% depleted fuel. An initial 5% loss in cell stack operating voltage, upon introduction of the sulfur species to the fuel stream, was (probably) caused by sulfur chemisorption on the nickel of the fuel electrode. Eliminating the sulfur impurity from the fuel gas resulted in a return to prior operating voltage by the cell stack.
5. Cell Stack #11, having variable cell lengths, operated at 800 mA/cm^2 (shorter length cell/rich fuel end of stack) to 200 mA/cm^2 (longer cell length, spent fuel end) and delivered 10.8 watts, at an average 0.57 V , at an average 400 mA/cm^2 , with a simulated coal-derived fuel ($\sim 40\% \text{ H}_2 / 60\% \text{ CO}$).
6. Series Stack #13, having a doped lanthanum-cobalt oxide cathode exhibited excellent initial performance, similar to stacks with indium oxide cathodes.
7. Series Stack #14, having praeosodymium oxide added to the doped lanthanum cobalt oxide, also displayed excellent initial performance.
8. The diffusion capability of porous support tubes is conveniently determined in a simple $\text{O}_2\text{-N}_2$ inter-diffusion test system.
9. DC testing and analysis indicate that non-linearities in the current-voltage characteristics of cells are due to fuel and oxidant transport processes (concentration polarization, fuel and air utilization).

10. AC testing and analysis shows considerable promise as a tool for examining cell polarizations by their time dependent behavior, as contrasted with DC testing, which is based on their non-linear V-I behavior.
11. Effective cell resistance at reduced temperatures (300-600°C) may be a useful indicator of cell electrolyte and cell electrical contact quality.
12. Diagnostic testing of cells at reduced temperature appears feasible. Further testing to correlate good and bad cell behavior at high temperatures with these tests is needed.
13. Computer analysis of cells, especially simulation tests, are useful for understanding cell behavior under operating conditions, and are essential for obtaining numerical estimates of cell parameters from experimental data.

4.0 THE PRESENT PROGRAM

The present program has been modified to address the critical aspects of the HTSOE fuel cell development. Work is now focussed on 4 major tasks in technology development:

- 1) Materials and processes advancement (including work on the support tube, air electrode and power contacts).
- 2) FBA cell-proof of design.
- 3) Module mock-up test.
- 4) Module design analyses.

5.0 OVERALL TECHNICAL EFFORT

Work on the program during this year concentrated in the areas:
1) support tube and air electrode advancement, 2) fuel cell stack testing under a variety of fuel and stack conditions, 3) stack tolerance to sulfur, 4) FBA cell advancement.

5.1 Technology Development

This task is concerned with materials and processes advancement. Specifically it involves the porous support tube, the air cathode and stack electrical contacting schemes.

5.1.1 Subtask 1A. Porous Support Tube Refinement

The FBA cell design requires a porous support tube with one end closed. The strength and porosity properties of the tube are essentially unchanged. Processing modifications required to fabricate the porous support tube for the FBA cell are under way.

Four refinements were implemented in the fabrication of the porous support tubes during this period.

1. Improvement in the quality of the extruded tubes by die modifications.

2. Improvement in the strength of the porous support tube by admixtures of the high- and low-temperature calcined material.

3. Fabrication of one end closed tubes by improved materials and processing techniques.

4. Lowering of the tube sintering temperature by modification of material processing techniques and minor additions.

5.1.1.1 Support Tube Fabrication

Support tube development work on one end closed tubes were phased-in by using materials, processes and fabrication techniques that were empirically established on open end tubes. The final materials and processes for the FBA cell porous support tubes will be selected on the basis of manufacturability and economic consideration.

5.1.1.2 Support Tube Experiments

Materials and processing experiments were performed on tailored admixtures of high- and low-temperature calcined calcia-stabilized zirconia (ZrO_2)_{.85} (CaO)_{.15} powders and also with some minor additions to obtain a stabilized, sintered zirconia body.

Extrusion

Modification of the extrusion die assembly with the redesigned "spider" resulted in high quality tubes of uniform wall thickness that can operate efficiently through a range of extrusion pressures. Figure 5.1 shows the modified barrel and other component parts that make up the extrusion die assembly. Figure 5.2 shows the extrusion die assembly with the plunger in position. The collar at the top of the assembly that includes the male hose connection is sealed around the plunger, to maintain vacuum, for deairing of the extrusion mixture, during the extrusion process.

Tailored Extrusion Batches

Experiments to determine the feasibility of tailoring admixtures of high- and low-temperature calcined material to improve strength and porosity characteristics were conducted on combinations of materials from 0-50 w/o. The results are shown in Table 5.1. The 50:50 admixtures showed the lowest porosity and the highest tensile strength in the group prepared for the experiment. Figure 5.3 shows the porosity and strength relationship of the different batches of admixtures, all fired at under the same conditions.

Support Tubes for the FBA Fuel Cell Design

A porous support tube that is straight, with one end closed, is a requirement of the FBA cell. Long straight porous support tubes with uniform wall thickness with one end closed have been fabricated, using tailored admixtures of calcia-stabilized zirconia.

Figure 5.1 - Support tube extrusion die -- component parts

Figure 5.2 - Assembled support tube extrusion die
(with plunger in position)

TABLE 5.1

Tensile Strength of Porous Support Tubes
Showing the Effects of Blending Starting Material
Calcined At Two Different Temperatures

<u>Sample</u>	<u>Ratio of H/L</u>	<u>Tensile Strength (psi)</u>	<u>Apparent Porosity (%)</u>
1	100%	3563	17.9 ± 3.0
2	100%	3189	19.4 ± 4.4
3	100%	2679	16.3 ± 3.7
4	100%	2072	17.6 ± 3.2
5	95/5	3424	22.3 ± 4.4
6	95/5	3343	22.2 ± 4.1
7	80/20	3574	14.7 ± 1.6
8	80/20	4601	15.6 ± 1.2
9	80/20	3252	16.1 ± 4.0
10	75/25	5123	15.2 ± 1.8
11	50/50	7440	8.4 ± 2.0

Note: H - Presintered at high temperature

L - Presintered at low temperature

All samples fired under the same firing conditions.

Fig.5. 3 - Tensile strength of porous support tubes showing the effects of blending starting materials calcined at two different temperatures

Figure 5.4 shows photographs of some tubes that have been made. Experimental results to date indicate that calcia-stabilized zirconia, $(\text{ZrO}_2)_{.85}(\text{CaO})_{.15}$, porous support tube material can be tailored to sinter at a lower temperature range by two methods: (1) employing admixtures of high- and low-temperature calcined materials and (2) by minor additions of sintering aids.

} Closed-end Tubes

} Closed-end Tubes

Figure 5.4. Samples of Open-End and Closed-End Calcia-Stabilized Zirconia Porous Support Tubes

5.1.1.3 Porous Support Tube Gas Transport Properties

An apparatus has been developed for the rapid measurement of both gas interdiffusion coefficients and gas permeation coefficients, within the porous support tubes. A knowledge of the gas interdiffusion coefficients makes it possible to predict porous support tube contribution to mass (fuel, combustion products) transport polarization at the fuel electrode of an operating stack. The gas permeation coefficients are also valuable, since they are sensitive indicators of pore size distribution of connected pores within these tubes.

Figure 5.5 shows a schematic of the apparatus in its present form. For a diffusion measurement, pure nitrogen flows through a section of porous tube (masking may be employed so that specific regions of the tube may be tested). Oxygen from the air diffuses through the tube wall pores into the nitrogen stream, where it subsequently can be measured by an oxygen gas analyzer at the exit of the porous tube. The differential pressure across the porous tube must, of course, be kept small to avoid a bulk viscous gas flow (permeation) through the tube wall. The effective interdiffusion coefficient is then calculated from:

$$D_{\text{eff}} = \frac{Sl}{A} \ln \left(\frac{pO_2}{pO_2 - p'O_2} \right) \quad (1)$$

where: D_{eff} = effective interdiffusion coefficient (cm^2/sec)

S = nitrogen flow rate (cm^3/sec)

l = tube wall thickness (cm)

A = tube wall area (cm^2)

pO_2 = oxygen partial pressure of air = 0.21 atm

$p'O_2$ = oxygen partial pressure measured by O_2 -analyzer (atm)

This D_{eff} , measured by the interdiffusion of N_2 and O_2 at room temperature, may be used in two ways: first, it provides a good relative indicator of how easily fuel and reaction products will interdiffuse through the porous

Fig. 5.5 -Schematic of apparatus for measuring gas interdiffusion coefficient and gas permeation coefficient of porous support tube

tube wall of an operating stack (high values of D_{eff} will correlate with low concentration overpotentials at the fuel electrodes) and second, it may be used to estimate the D_{eff} for other gases and for other temperatures, pertinent to actual fuel cell operation. For example, it can be shown that, to a good approximation*

$$D_{\text{eff}} (\text{H}_2\text{-N}_2, 1000^\circ\text{C}) = D_{\text{free}} (\text{H}_2\text{-N}_2, 1000^\circ\text{C}) \times \left[\frac{D_{\text{eff}} (\text{O}_2\text{-N}_2, 23^\circ\text{C})}{D_{\text{free}} (\text{O}_2\text{-N}_2, 23^\circ\text{C})} \right] \quad (2)$$

The quantity in brackets is essentially a reduction factor which can be used to convert free gas diffusion coefficients (available in the literature) into effective diffusion coefficients for a specific porous tube material. For currently tested porous tubes this factor ranged from about 0.025 to 0.033. From the literature, one can find values for the free gas diffusion coefficients:

$$\begin{aligned} D_{\text{free}} (\text{H}_2\text{-N}_2, 1000^\circ\text{C}) &= 9.8 \text{ cm}^2/\text{sec} \\ D_{\text{free}} (\text{H}_2\text{O-N}_2, 1000^\circ\text{C}) &= 3.2 \text{ cm}^2/\text{sec} \\ D_{\text{free}} (\text{H}_2\text{-H}_2\text{O}, 1000^\circ\text{C}) &= 10.9 \text{ cm}^2/\text{sec} \\ D_{\text{free}} (\text{O}_2\text{-N}_2, 1000^\circ\text{C}) &= 2.6 \text{ cm}^2/\text{sec} \end{aligned} \quad (3)$$

Application of the reduction factor mentioned above to these values then yields estimates for effective diffusion coefficients for porous tube material currently in use:

$$\begin{aligned} D_{\text{eff}} (\text{H}_2\text{-N}_2, 1000^\circ\text{C}) &\approx 0.24 \text{ to } 0.32 \text{ cm}_2/\text{sec} \\ D_{\text{eff}} (\text{H}_2\text{O-N}_2, 1000^\circ\text{C}) &\approx 0.08 \text{ to } 0.11 \text{ cm}^2/\text{sec} \end{aligned}$$

*This calculation assumes that the diameters of the pores are much greater than the mean free path of the diffusing molecules, which is believed to be valid for the porous materials considered here.

$$D_{\text{eff}} (\text{H}_2\text{-H}_2\text{O}, 1000^\circ\text{C}) \approx 0.27 \text{ to } 0.36 \text{ cm}^2/\text{sec}$$

$$D_{\text{eff}} (\text{O}_2\text{-N}_2, 1000^\circ\text{C}) \approx 0.07 \text{ to } 0.08 \text{ cm}^2/\text{sec}$$

These values are useful for estimating the contribution of the porous support tube to electrode concentration polarization.

The gas permeation coefficient, K , which measures the viscous flow of gas through the porous tube walls under a finite pressure difference, may also be measured in the apparatus. As shown in Figure 5.5, the closing of a single valve in the system leads to a differential gas pressure, ΔP , across the specimen tube wall. Then,

$$K = \frac{S\ell}{A\Delta P} \quad (5)$$

where: K = nitrogen permeation coefficient $\left(\frac{\text{cm}^2}{\text{sec}} \text{ in } \text{H}_2\text{O}\right)$

S = nitrogen flow rate (cm^3/sec)

ℓ = tube wall thickness (cm)

A = tube wall area (cm^2)

ΔP = differential pressure across tube wall (in. H_2O)

The permeation coefficient is a useful tool for comparing the quality of porous support tubes because it is especially sensitive to the number and size of the larger pores, as well as any pinholes or cracks. This can best be appreciated by noting that the permeation through a given pore is proportional to the fourth power of its diameter.*

For a more detailed and graphic method of investigating the distribution of pore sizes in support tubes, a bubble permeation apparatus was constructed. This system is shown schematically in Figure 5.6. Immersion of the specimen in water effectively blocks the gas at the exits of the pores at low differential pressures. As this pressure is

*In contrast, diffusion through a pore is proportional to the square of its diameter.

Fig. 5. 6-Schematic of apparatus for measurement of partial permeation coefficients and the distribution of pore sizes.

gradually raised, the surface tension of the water blocking the pores is overcome, starting with the largest pores first. Specifically, gas will bubble from those pores whose exit diameters, d , satisfy the condition

$$d \geq \frac{4\sigma}{\Delta P} \quad (6)$$

where: d = exit diameter of pores (cm)

σ = surface tension of water = 72 dynes/cm

ΔP = differential pressure across tube wall and water-gas interface at pore exit (dyne/cm²)

Analogous with the ordinary gas permeation coefficient, K , one can define a "bubble permeation coefficient," K_B , given by

$$K_B = \frac{S\ell}{A\Delta P} \quad (7)$$

Furthermore, by taking the difference between the bubble permeation coefficients measured at two different ΔP 's, one may obtain a "partial bubble permeation coefficient", ΔK_B , corresponding to one particular range of pore sizes.

For measurement of the nitrogen flow rate, S , one has two options: (1) a flowmeter, whose readings must be corrected for the effect of pressure, ΔP , or (2) the timed collection of gas in a burette, which is the method employed in our apparatus. In preliminary experiments we have used narrow bubble collectors in order to make it possible to scan specific areas along the porous tube.

Although bubble permeation coefficients provide a useful relative measure of pore size effects, they are strongly influenced by the back-pressure required for bubble formation. They may, therefore, be expected to differ greatly from the true gas permeation coefficients, discussed earlier, which are controlled entirely by viscous flow effects in the pores.

5.1.2 Subtask B. Air Electrode Development

Tin-doped indium oxide has previously performed satisfactorily as the air electrode current carrier. Although it has been used to produce cell stacks that have performed satisfactorily (for up to 500 h at 1000°C without degradation)⁽¹⁾, indium oxide, when used, represents both the most costly and least thermodynamically-stable component in the HTSOE fuel cell. Also it is not well adapted to survive the EVD processing steps required for the FBA cell design. Therefore, it is desirable to replace this oxide with another material.

We have previously reported on work using a mixed oxide -- strontium-doped lanthanum manganite -- as an air electrode. A series-cell stack, using a sintered electrode of this material, gave a steady performance in a seven day test that involved four thermal cycles (RT-1000°C-RT). However, the power performance goal (in terms of W/cm^2 of electrode area) was not met by this stack, apparently, due to a higher-than-anticipated resistance of the air electrode or its interface with the electrolyte. Therefore, we have been investigating the basic conductivity and thermal expansion properties of other mixed oxides, as well as other substitutions in the lanthanum manganite, with the goal of obtaining an alternate air electrode and could be used to produce a cell with improved performance in the FBA design.

Physical and chemical properties required of mixed oxides to be suitable as air electrode materials include: (1) high electronic conduction in an air atmosphere (greater than $10^2 \text{ (ohm-cm)}^{-1}$; (2) no reaction with other cell components with which it is in contact at the operating temperature of $\sim 1000^\circ\text{C}$; (3) very low volatilization in air; (4) low electrode polarization characteristics and (5) a thermal expansion that closely matches that of the zirconia-based support tube.

The first three property requirements are very rigid. Property (4) can be realized by the use of depolarizing additions of praseodymium cobalt oxide and other materials. In the case of (5), special techniques for producing crack resistance mosaic structures (with second phase additives) may, perhaps, be helpful, if a close expansion match cannot be attained.

Table 5.2 compares thermal expansions of some typical, high conductivity mixed oxides that have been used here, and elsewhere, as air electrode materials.

TABLE 5.2
THERMAL EXPANSION DATA OBTAINED ON VARIOUS
CANDIDATE AIR ELECTRODE MATERIALS

<u>Air Electrode Material</u>	<u>Thermal Expansion $\text{mm}^{-1}\text{°C}^{-1}$ 25 to 1000°C</u>
$\text{In}_{1.96}\text{Sn}_{.04}\text{O}_3$	9×10^{-6}
$\text{La}_{.9}\text{Sr}_{.1}\text{MnO}_3$	11×10^{-6}
$\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$	$10 - 14 \times 10^{-6}$
LaCoO_3	23×10^{-6}
$\text{La}_{.9}\text{Ca}_{.1}\text{CoO}_3$	20×10^{-6}
LaNiO_3	14×10^{-6}
$(\text{Y}_2\text{O}_3)_{.1}(\text{ZrO}_2)_{.9}$ electrolyte	10.5×10^{-6}
$(\text{CaO})_{.15}(\text{ZrO}_2)_{.85}$ support tube	10.0×10^{-6}

Several of these oxides (with the formula ABO_3) have a perovskite-like crystal structure, where A consists of large ions such as La^{3+} or Sr^{2+} which, with the O^{2-} ions, form an ordered cubic close packed structure. The small B ions (e.g., Mn^{3+} , Ni^{3+} , Co^{3+}) occupy the octahedral positions, coordinated to six oxygen ions. Relatively high conductivities are possessed by some of these materials (i.e., in the range 10^{-2} to 10^{-4} ohm cm at 1000°C).

Earlier measurements had suggested that lanthanum manganite properties could be tailored to give electrical conductivity and thermal expansion properties suitable for the air electrode application by substitution of Sr^{2+} or Ca^{2+} for part of the La^{3+} . Three types of measurements have been made:

(1) thermal expansion measurements in the systems $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, (2) resistance changes as a function of temperature and oxygen partial pressure and (3) oxygen loss from $\text{La}_{.5}\text{Ca}_{.5}\text{MnO}_{3-x}$ in atmospheres with lower oxygen partial pressures than in air (the normal cathode atmosphere). The measurements were made using a high temperature microweighing system previously described. (2)

5.1.2.1 Thermal Expansion of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$

Figures 5.7 and 5.8 show thermal expansion curves of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ compositions, respectively, for temperatures between 25° and 1350°C. The samples were pretreated at 1350°C for 64 hours in air. The values vary with composition. The compositions $\text{La}_{1-x}(\text{Sr or Ca})_x\text{MnO}_3$, with $x \approx 0.2 - 0.3$, have thermal expansion values comparable to the yttria-doped zirconia electrolyte ($\sim 10-11 \times 10^{-6}$ m/m/°C from 25 - 1000°C) and should be suitable from this standpoint.

In the case of the calcium substituted compositions a crystal transformation occurred during the thermal expansion measurement between 1400-1500°C as shown in Figure 5.9 for $\text{La}_{.7}\text{Ca}_{.3}\text{MnO}_3$. Sample shrinkage occurring in the vicinity of the transformation temperature of this oxide is typical of these materials and is apparently due to accelerated ionic diffusion, known to occur in many ionic solids near a transformation point.

5.1.2.2 Electrical Conductivity of Lanthanum Manganites

Lanthanum manganite is an intrinsic conductor at 1000°C. However, its resistivity can be decreased further by substituting calcium or strontium for part of the lanthanum. This is illustrated in Figure 5.10 which compares resistivities of pure and two substituted lanthanum manganites as a function of temperature.

Near 1000°C the resistivities of pure, as well as calcium or strontium substituted lanthanum manganites increase with temperature, a characteristic typical of metallic conductors in which the number of charge carriers remain essentially constant as the temperature changes, and the electronic

Fig. 5.7—Thermal expansion of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$

Fig. 5.8—Thermal expansion of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$

Curve 728479-A

Fig. 5. 9—Thermal expansion of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ showing phase transformation

Fig. 5. 10—Resistivity of pure and substituted lanthanum manganite

mobility is not activated. At temperatures below 950°C for LaMnO_3 and 500°C for $\text{La}_{.5}\text{Ca}_{.5}\text{MnO}_3$, conductivity becomes more typical of a semiconductor in having a negative temperature coefficient (i.e. conductivity increases with temperature).

Resistivities at 1000°C decrease in the system $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, until x reaches about 0.7, as shown in Figure 5.11. However, thermal expansion requirements appear to limit the practical application of this system as an air electrode to compositions near $x \approx 0.2 - 0.3$.

5.1.2.3 Oxygen Loss from $\text{La}_{.5}\text{Ca}_{.5}\text{MnO}_3$

The diffusion of oxygen in perovskite structure oxides is a few orders of magnitude slower than in the zirconia-based electrolyte. As a consequence, when an oxide with this crystal structure, such as $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, is used as the air electrode, any nonporous areas of the electrode-electrolyte interface, to which the access of oxygen is possible only by a solid state diffusion mechanism, may encounter an effective oxygen pressure somewhere between that of the air at the cathode and that of the fuel electrode. Should this effective pressure be sufficiently low at any point, oxygen would be lost from the crystal lattice structure near the location. The result, in such a case, would be an increase in resistivity of the oxide near the region of oxygen loss. This could perhaps result in significant polarization being associated with the air electrode.

To determine the oxygen partial pressures in $\text{La}_{.5}\text{Ca}_{.5}\text{MnO}_3$ that would be required to produce such oxygen loss, we suspended a porous sample of this oxide in a high-temperature, controlled atmosphere microweighing system. Weight loss at various oxygen partial pressures for oxygen/nitrogen/water vapor, and water/hydrogen/nitrogen mixtures was measured at 1000°C. Some results are illustrated in Figures 5.12 and 5.13. The solid lines in Figure 5.12 are calculated from equation 1 below, using two values of $\log K_t^2$:

$$\log P_{O_2} = 2 \log \left[\frac{(3-x)(y-2x)^2}{x} \right] - \log K_t^2 \quad \text{Eq. 1}$$

Fig. 5.11—Fraction, x , substitution for La in $\text{La}_{1-x}\text{M}_x\text{MnO}_3$

Fig. 5.12—Oxygen loss from $La_{0.5}Ca_{0.5}MnO_{3-x}$ vs. O_2 partial pressure

where K_t is the equilibrium constant at the specified temperature t and y and x are, respectively, the moles of Ca^{++} in the oxide and $\text{O}^{=}$ lost from a mole of $\text{La}_{.5}\text{Ca}_{.5}\text{MnO}_{3-x}$, for the solid state equilibrium with gaseous oxygen, given in equation 2 below:

In this equilibrium $\square^{\text{O}^{=}}$ is an oxygen ion vacancy, assumed to be equal to the oxygen loss, x , from the crystal lattice in Equation 1, h^{+} is a positive hole charge carrier assumed to be equal to $(y - 2x)$, and $\text{O}^{=}$ is a normal, doubly-charged oxygen ion in the oxide.

In oxygen or air the composition is close to stoichiometric $\text{La}_{.5}\text{Ca}_{.5}\text{MnO}_3$. At 10^{-4} atmospheres it begins to lose a small amount of oxygen and the composition is about $\text{La}_{.5}\text{Ca}_{.5}\text{MnO}_{2.995}$, as indicated in Figure 5.12.

As oxygen is lost the crystal structure may undergo an expansion as has been noted for the corresponding case of another perovskite-like oxide, $\text{La}_{.75}\text{Sr}_{.25}\text{CrO}_{3-x}$ by others. This effect is, presumably, the result of localized expansions around the individual sites vacated by the oxygen ions, due to an accompanying net loss in the coulombic attractive energy portion of the lattice energy. As the lattice undergoes such expansion, the value of K_t in equation 1 might also be expected to change somewhat. Such effect is suggested by an apparent gradual increase in the value of $\log K_t^2$ as shown in Figure 5.13.

Although equation 1 appears to be adequate as a simple working calculation to correlate the oxygen loss data at 1000°C , it involves certain questionable assumptions. These include: (1) that equation 1 is an adequate approximation to the solid state equilibrium, without the need to involve chemical activity coefficients and interactions of possible localized charge complexes, or locally ordered domains, within the solid; (2) that the number of positive hole charge carriers, h^{+} , is equal to the number of Ca^{++} ions in the fully oxygenated oxide ($x = 0$) and (3) that the number of negative charge carriers can be neglected.

Curve 727260-A

Fig. 5.13- Change of equilibrium constant with oxygen partial pressure for interaction of oxygen with $La_{0.5}Ca_{0.5}MnO_{3-x}$

These assumptions are not obvious because pure LaMnO_3 is an intrinsic conductor at 1000°C with a resistivity that is higher than, but within a factor of four, of $\text{La}_{.5}\text{Ca}_{.5}\text{MnO}_3$. It is reasonable to anticipate, however, that such a large substitution of Ca^{++} will introduce enough additional positive hole charge carriers to suppress the negative component which is, presumably, coexistent with the positive component in the pure LaMnO_3 composition. On the other hand, at higher temperatures the negative carrier component might again become significant.

A reasonable interpretation of the nature of the electronic conductivity of $\text{La}_{.5}\text{Ca}_{.5}\text{MnO}_3$ up to 1000°C is perhaps given in terms of delocalized charge carriers, most of which are positive holes. Since the concentration of Ca^{++} ions and positive hole charge carriers is so high, there is no apparent reason to suggest that any localized charge complex equilibria be involved in equilibrium Equation 2. This contrasts with earlier work with relatively dilute substitutions of Mg^{++} or Sr^{++} in another perovskite-like compound, LaCrO_3 , a compound which, in contrast, does not show a high intrinsic conduction in the pure form.

These data show that little oxygen is lost from $\text{La}_{.5}\text{Ca}_{.5}\text{MnO}_3$ until the oxygen pressure is many orders of magnitude less than that in air at 1000°C , the approximate operating temperature of the zirconia electrolyte fuel cell. This suggests that little of the electrode polarization, attributable to air electrodes of this material, should result from oxygen loss from the oxide, as long as the electrodes are sufficiently porous. This suggestion is further confirmed by measurements of the resistance of porous slabs of this oxide as a function of oxygen partial pressure. These measurements show very little change in electrical resistance at 1000°C for oxygen pressures between 0.21 atm and 10^{-4} atm.

5.2 Fuel Cell Stack Advancement

This task deals with the fabrication and test evaluation of fuel cell stacks under a variety of simulated service conditions. Here effects of those conditions will be determined on individual components and interfaces. Also a mathematical treatment of fuel cell structural and operational characteristics will be attempted.

5.2.1 Subtask A. Bench Testing of Stacks Under Simulated Service Conditions

During the past year series-cell stacks were tested to evaluate sulfur tolerance conditions. Also FBA cells were constructed and evaluated to establish the state-of-the-art of these cells, as compared with the performance obtained in the cells in the series-cell stacks.

5.2.1.1 Sulfur Tolerance of Stack #8

A 10-cell stack operated for 2000 h at 400 mA/cm^2 , using hydrogen fuel. ⁽³⁾

For the next 300 h of operation, the fuel was changed to a CO/H_2 mixture, diluted with CO_2 , corresponding to an exit gas mixture of 85% to 88% fuel depletion. The current was reduced to 150 mA/cm^2 , to avoid oxidizing the nickel anode. During the last 800 h of testing, a mixture of nitrogen, doped with H_2S , was injected into the lean fuel gas, up to a level of 50 ppm H_2S . Seven of the 10 cells operated continuously under this fuel condition at 150 mA/cm^2 . The effect of sulfur upon the stack terminal voltage is seen in Figure 5.14. A relatively fast deterioration of voltage occurred during the first few hours. However, voltage stabilized at about 95% of the operating value (before H_2S was introduced into the fuel gas stream). Upon elimination of H_2S , the stack nearly returned to the prior operating voltage. This reversibility suggests that sulfur chemisorption is occurring which partially retards fuel oxidation, probably by blocking active electrode reaction sites. Sulfidation of the electrode was not observed by post operation examination of this stack.

Fig. 5.14 – Sulfur tolerance test on test stack No. 8

5.2.1.2 Sulfur Adsorption on Nickel

To examine the possibility of a pressure dependent absorption of H_2S , S_2 or SO_2 species on nickel, we subjected a porous sintered nickel powder electrode material to a hydrogen/water fuel gas mixture, containing sulfur gas species at concentrations from about 30 to 140 ppm, in the high-temperature microweighing system. Changes in sample weight were measured at a hydrogen-to-water ratio corresponding to an open circuit fuel cell voltage of about 0.712 volt in the gas mixture ($\text{H}_2 + \text{H}_2\text{O} = 0.40$ atm plus $\text{N}_2 = 0.56$ atm). Under these conditions thermodynamic data suggest sulfidation above 115 ppm. Present experimental data show sulfidation at 130 ppm and desulfidation at 105 ppm total sulfur, as expected for an initially sulfided sample. For an unsulfided nickel sample, on the other hand, a continuous weight gain was observed at 130 ppm, while at 105 ppm, or less, of sulfur containing gases, a maximum weight gain was attained after about 4 hours.

Due to gradual sintering that occurred at 1000°C, we do not know the actual surface area of nickel. However, an estimate based on the initial particle size and assumption of a smooth particle surface suggests that sulfur uptake (based on weight gain of the nickel at 110 ppm sulfur containing gases) is within a factor of three of that required for monolayer coverage. Figure 5.15 shows sulfur gas uptake as a function of time at different sulfur-containing gas concentration levels. Note the limiting value of sulfur uptake in the "absorption" region. Continuous weight gain takes place in the region above ~115-125 ppm, where true sulfidation occurs.

To convert the $\text{H}_2/\text{H}_2\text{O}/\text{SO}_2$ feed gas to the equilibrium $\text{H}_2/\text{H}_2\text{O}/\text{SO}_2/\text{H}_2\text{S}$ mixture for these experiments, the mixture was passed through a platinum impregnated alumina wool plug at the nickel sample temperature of 1000°C. Without this precatalysis step, higher SO_2 concentrations are required in the feed gas to sulfidize the nickel, presumably due to very slow and incomplete conversion of SO_2 to the equilibrium $\text{SO}_2/\text{H}_2\text{S}$ mixture on the nickel electrode itself. This suggests caution in interpreting results of tests on fuel cell stacks in those cases where appreciable conversion of the added sulfur gas is required to attain equilibrium at the operating temperature.

Fig. 5. 15- Adsorption at 1000°C of sulfur-containing gas species on nickel powder bar, presintered at 1000°C in 7% H_2 /93% N_2

For a small amount of sulfidation the molten nickel sulfide is retained in the pores of a sintered nickel powder bar sample and the sulfidation and desulfidation rate can be repeatedly examined without disintegration of the bar in the controlled atmosphere micro-weighing system. Figure 5.16 of the sulfidation/desulfidation behavior of such an Ni/NiS_x two phase sample bar. The weight change of the sample per hour is seen to be nearly proportional to the total sulfur gas pressure minus the sulfur pressure at which the two phase Ni/NiS_x exists. These data suggest that a small overpressure of sulfur gases for short periods of time will not cause a nickel electrode to fall apart and, perhaps, will have minimal effect on operation, once the nickel sulfide is reduced back to nickel, when normal operation of the stack is restored.

Fig. 5.16 - Rate of sulfidation and desulfidation at 1000°C of sintered nickel powder bar. Bar 0.4 g suspended in controlled atmosphere microweighing system and partially presulfided.

5.2.1.3 Sulfur Impurity - Thermodynamic Considerations

Under equilibrium conditions, the tolerance of nickel fuel electrodes to sulfidation by sulfur-containing impurities in the fuel gas depends on the H_2/H_2S or CO/COS ratio. For a given partial pressure of sulfur-containing gas species, these ratios depend on the fuel composition, temperature, oxygen partial pressure in the fuel (related to open circuit fuel cell voltage) and the total gas pressure. A minimum tolerance to sulfidation for coal-derived gases, containing, largely, CO , H_2 , CO_2 and H_2O , occurs in the general region of 0.70-0.75 V, at temperatures between 700°-1000°C and one atmosphere total pressure. In the region near this minimum the $(H_2S + COS)$ and SO_2 contents of the fuel gas are of similar magnitudes, whereas, at lower voltages, SO_2 predominates and, at higher voltages, both H_2S and COS are the predominating sulfur-containing species. Graphs illustrating this behavior were given in a previous report.⁽³⁾

Figure 5.17 shows one illustration of such a minimum, for a nickel anode material, using a fuel containing hydrogen diluted with nitrogen. The solid curve is calculated from thermodynamic data, while the experimental points were obtained using a high-temperature, controlled atmosphere, microweighing system. Calculated minimum tolerance values of this type for a variety of temperatures and fuel compositions are plotted in Figure 5.13. Practically, sulfur concentrations should be kept well below these limiting values to prevent physical damage to the nickel cermet fuel electrode structures, since nickel sulfides are molten at the operating temperature (~1000°C) of the HTSOE fuel cell stack.

Figure 5.19 shows calculated values of the open circuit voltages at which minimum tolerance to sulfidation occurs for any $(H_2 + H_2O)$ to $(H_2 + H_2O + CO + CO_2)$ ratio (i.e., volume % $(H_2 + H_2O)$ in the fuel stream) from 700° to 1100°C. These voltages are lower at higher % $(H_2 + H_2O)$.

As the fuel mixture passes through the operating fuel cell stack, the H_2 and CO partial pressures decrease, as do the amounts of H_2S and COS . On the other hand the amounts of S_2 (very small) and SO_2 increase, until the minimum tolerance voltage point is passed and S_2 begins to

Fig. 5.17 — Tolerance of nickel to sulfidation in $H_2/H_2O/N_2$ atmosphere at 1000°C

Fig. 5.18 - Minimum tolerance of nickel electrodes to sulfidation as a function of fuel gas composition

Fig. 5. 19— Voltage at which minimum tolerance to sulfidation occurs as a function of fuel composition and temperature (Thermochemical calculations)

decrease. If the S_2 pressure exceeds the values of the dissociation pressure of S_2 over NiS_x , then the nickel will sulfidize. However, if complete equilibrium is not attained, the sulfur level at which actual sulfidation occurs may differ from the calculated values or those values obtained experimentally under near-equilibrium conditions. Experiments with fuel cell stacks, under different simulated conditions of flow rate, fuel composition, temperature and other variables, will be done to evaluate such possible effects.

5.2.1.4 Bench Testing of Cells

Two types of fuel cells have been under investigation during the past year. One is a multi-cell stack arrangement, as reported on during previous report periods, the other consists of a tubular cell with an inverted cell geometry, designated as an FBA cell. For the FBA cell, the fuel electrode is on the outside, for simplified contacting with metallic conductors in the reducing fuel environment. The status of constructing and testing both types of cells is now described.

5.2.1.4.1 Bench Testing of Multi-Cell Stacks

Eight stacks have been fabricated this past year. Stack #12 broke during the final phase of fabrication and was not tested. Stack evaluation was conducted with two major objectives: (1) to establish stack performance under fuel conditions that can be expected in actual generators, namely, consumption of fuel up to 90%, and (2) to test new air electrode materials.

Stack #11 Performance

To achieve high fuel consumption at a high current density, certain structural changes had to be made in the series cell stack configuration. Test results of Stack #8 indicated that fuel electrodes cannot operate at a current density higher than, approximately, 200 mA/cm^2 , using a 90% depleted, modified coal gas.⁽⁵⁾ Therefore, Stack #11 was constructed, having shorter-length cells at the fuel inlet and longer-length cells at the fuel outlet. The overall ratio was 1:4 for the lengths of these cells. Since these cells are electrically series-connected, this construction can achieve a high average current density (of 400 mA/cm^2) with high fuel consumption in the overall cell stack. Here the shorter cells, exposed to rich fuel conditions, can operate at high current densities (800 mA/cm^2 , or higher) while the downstream cells in the spent fuel region can operate at a lower current density ($\sim 200 \text{ mA/cm}^2$). Figure 5.20 presents the stack performance characteristic. Curve 1 was obtained with a fuel flow of $600 \text{ ml H}_2/\text{min}$; curve 2 represents the performance using a simulated, coal derived fuel gas and a flow of 600 ml/min . Nearly complete fuel combustion was achieved by

Curve 725297-B

Fig. 5.20-Performance of cell stack No. 11, having variable length cells

reducing the fuel gas flow to 134 ml/min fuel gas and operating the stack at a current of 800 mA. Here the first cell operated at a current density of 800 mA/cm^2 and the last one at 200 mA/cm^2 . Curves 3 and 4 show the performances at the lower gas flow rate. Due to the inaccuracy of fuel gas flow adjustment, the actual fuel flow was nearly 10 percent higher, as determined by the potential of cells exposed to the exit fuel gas. The vertical line in Figure 5.20 indicates the point of nearly complete combustion. The operating stack voltage was constant at this current. Further current increase lead to stack performance loss, due to nickel anode oxidation. The stack delivered 10.8 watts, using a simulated coal-derived fuel at an average current density of 400 mA/cm^2 and nearly 90% fuel consumption. The average cell voltage was $0.57 \bar{V}$. The performance goal of future cells is $0.60 \bar{V}$, under similar conditions.

Stack #13 Performance

This 24-cell stack was fabricated with doped lanthanum-cobalt oxide cathodes that were applied by flame-spraying. This oxide has a considerably higher coefficient of thermal expansion ($20 \times 10^{-6}/^{\circ}\text{C}$) than calcia-stabilized ZrO_2 ($10 \times 10^{-6}/^{\circ}\text{C}$). One can expect that multiple temperature cycling could lead to cathode flaking. No flaking occurred, however, when cooling the stack from the flame spray temperature of nearly 900°C down to RT, nor did one complete temperature cycle during testing affect the stack performance. The porous electrode was impregnated with cobalt-praseodymium oxide. Figure 5.21 shows the initial cell characteristic, as well as that after 360 hours of operation.

This is the first stack that exhibited excellent performance, using other than the standard, composite oxide cathode. This is of great significance in the development of less complicated and, potentially, less costly air electrodes. Since indium oxide is the most expensive stack component material, one would like to substitute it for less costly oxides. However, other known electrically conducting oxides compare unfavorably with doped indium oxide, as far as conductivity is concerned. It is expected, therefore, that such oxides must be applied in thicker

Fig. 5.21- Performance of cell stack #13

layers (100 to 600 μm) to obtain equivalent conductivity. An increase of air electrode polarization can be a result of thicker air electrodes, unless the degree and tortuosity of the porous structure are carefully controlled.

During the operation of Stack #13, a performance decay was observed as shown in Figure 5.22. This was analyzed as cell shorting, caused by platinum vapor deposition between cells, stemming from the platinum screen contacts. Platinum oxide vapors are reduced on cathodes and form platinum metal coatings at high cell currents and limited oxygen supply. The deterioration of open stack voltage was also observed, as a result of this shorting.

Stack #14 Performance

To reproduce Stack #13 performance, 20-cell Stack #14 was equipped with $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ cathodes. Figure 5.23 shows the stack characteristic. The performance was equivalent to that of Stack #13. The oxygen (air) flow was increased, to avoid depositing platinum, and no deterioration of open stack voltage occurred, even after high current operation, as was observed in operating Stack #13. A characteristic taken with a current limiting flow of fuel (mixture of 35% H_2 , 65% CO) indicates that fuel starvation sets in at ~85% fuel consumption. This is not surprising, since the last cells of the tubular stack operate at a very lean fuel mixture, yet operate at the same current density as cells located near the fuel inlet. Cell sizing, as done in cell Stack #11, would greatly improve the overall stack performance under such conditions.

It can be concluded from these tests that modified lanthanum cobalt oxide, impregnated with praseodymium cobalt oxide, is an excellent cathode material, as evidenced by its reproducible fabrication and performance in cell Stacks #13 and #14.

Stack #15 Performance

This 23-cell stack also was fabricated using the flame-spraying technique for cathode application. The oxide material was $\text{La}_{.5}\text{Ca}_{.5}\text{MnO}_3$.

Curve 726554-A

Fig. 5.22 — Performance of cell stack #13 as a function of time at temperature (1000°C)

Fig. 5.23—Performance of cell stack #14

Cobalt praseodymium oxide was added, via nitrate solution impregnation and subsequent thermal decomposition. Figure 5.24 shows stack electrical behavior. Performance decrease was observed when air was used as the oxidant; with oxygen, however, the performance was remarkably stable. This indicates that air electrode polarization losses were exclusively responsible for degradation. This is significant, since it indicates that no short term deterioration (144 hours) is expected between this cathode material and lanthanum chromite interconnection. This finding confirms the results obtained with a sintered manganite cathode (Stack #5) which showed a more stable performance in air, although at a lower current density. This behavior suggests that a better control over porosity in the electrode structure is essential, to increase performance.

Due to the reproducibility in fabrication of all other stack components, it is now possible to associate stack performance more closely with that of cathode behavior. The use of higher and lower concentrations of oxygen than that in air will help to characterize electrode mass transport properties.

Performance of Stacks #16, #17, and #18

Lanthanum nickel oxide (LaNiO_3), in pure and doped form, is another potential cathode material. A first test of the effectiveness of a flame sprayed cathode was made in Stack #16, using calcia-doped oxide, see Curve 1 in Figure 5.25. Performance was stable but low. Considerable improvement was achieved by using pure oxygen (Curve 2) instead of air, which hints to insufficient porosity, due to the method of application. However, it was also observed in current-interruption studies that lower cathode resistance contributed to improved performance when operated in oxygen. Sluggish recovery in going from oxygen-rich to oxygen-poor cathode gases, and vice versa, suggests that bulk oxide equilibration with the atmosphere plays a part in the polarization and conduction behavior of this oxide material. Similar effects were observed in testing of Stack #18 which employed titania-doped lanthanum nickel oxide cathodes, as shown in Curve 4, Figure 5.25.

Fig. 5.24 — Performance of stack #15

Fig. 5.25 — Performance characteristics of cell stacks 16, 17, 18

Stack #17, an 18-cell stack, was equipped with strontium-doped lanthanum manganite cathodes which were flame-sprayed onto the stack. Performance was equivalent to that of Stack #16.

Conclusions on Multi-Cell Stack Tests

The virtually trouble-free fabrication of multi-cell stacks demonstrates reliability in processing of tubes, fuel electrodes, electrolyte and interconnection. Test stacks look unchanged after prolonged operation, which is indicative of the absence of structural flaws. Furthermore, stacks can be subjected to rigorous handling, with respect to heat treatment, as demonstrated by successful application of various oxide cathodes by flame spraying. Considerable experience has been gained in this technique and significant improvements can be expected, leading to better cathodes of lower cost materials than those electrodes that incorporate indium oxide.

5.2.1.4.2 Bench Testing of FBA-Type Cells

The FBA cell comprises a design in which the air flows inside the support tube and the fuel flows outside the tube. This means that the fuel and air electrodes are in reversed positions, as compared with the multi-cell stack.

The first HTSOE fuel cell of the FBA type was tested, where electrical contacts to the electrodes were made in a reducing (fuel side) environment. Contact material was nickel metal (no noble metal was used for any electrical contact). The performance of this cell is shown in Figure 5.26. The test fuel was wet (25°C H₂O) hydrogen. Cell Characteristics A and B in Figure 5.26 were obtained with air and pure oxygen, respectively. The cell showed one of the highest open cell potentials ever observed on a thin film zirconia cell with an incorporated interconnection. Performance and open cell voltage were constant for several days. The low current density of this cell is probably due to an air electrode-electrolyte interface problem, which could be expected, since no effort was made to structure this important contact zone. Later experiments will deal with refining of this electrode/electrolyte interface structure, to improve FBA cell performance.

Curve 727761-A

Fig. 5. 26—Performance of first FBA fuel cell

The important result of this first FBA cell test is the fact that all fabrication processes, identified in the past program, can be applied to this cell structure, without major complications appearing. Also, the potential of modified lanthanum manganite, to replace the less stable and expensive indium oxide as the air electrode current collector, has been demonstrated.

Follow-on FBA cell experiments dealt with refining EVD parameters, as well as "tailoring" the interface between the electrolyte and the air electrode. Here, both structural, as well as compositional modifications of the interface, were under consideration. Other efforts dealt with the air electrode composition, to improve both its thermal expansion and electrical conductivity.

The FBA cell introduces other parameters that deserve attention. The air electrode, consisting of thicker layers of mixed oxides (to replace expensive but more conductive In_2O_3) is adjacent to the porous support tube. Both, porous tube and air electrode, represent a diffusion barrier for oxygen delivery to the cathode/electrolyte interface. In order to test the effects of tube and electrode porosity on cell performance, we have conducted half-cell tests, where oxygen is pumped (electrochemically) through the air electrode-electrolyte sandwich, backed up by the porous support as an oxygen diffusion barrier. Data obtained by these tests are indicated in Figure 5.27, where curve A was produced with a test cell in air and at 1000°C , when oxygen access to the air electrode was severely restricted by a low porosity porous support tube ($\sim 15\%$ pores, 1.5mm thickness) and a low porosity air electrode ($\sim 10\%$ pores, 0.6mm thickness). Here a current limitation of near $250\text{mA}/\text{cm}^2$ occurred. The introduction of pure oxygen eliminated the diffusion barrier effect and curve B was obtained. After mechanical removal of most of the porous support tube in the same cell (the air electrode supports this "thin" cell), curve C showed the current limitation in air with, essentially, only the air electrode as a diffusion barrier.

Fig. 5. 27— Air electrode half cell tests

Higher porosity support tube/air electrode combinations have been fabricated and curve D shows a current voltage characteristic obtained with a tube/air electrode porosity of near 30 vol % and a combined sandwich thickness of ~21mm, as in the previous case. An improvement of current limitation by a factor of three was obtained (compare curve A with D). Further reduction in thickness of both the porous support tube (1mm) and the air electrode (~0.4mm) will, ultimately, increase the practical limiting current to over $800\text{mA}/\text{cm}^2$, while maintaining the porosity level of the support near 30 vol %.

5.2.1.5 Diagnostic Fuel Cell Testing at Reduced Temperatures

There is considerable potential value in testing HTSOE fuel cells at relatively low temperatures (approx. 25°C to 500°C), as a quality control test, rather than at their normal operating temperatures (approx., 900° to 1100°C). For this reason a number of experiments have been initiated to examine the electrical characteristics of cells at reduced temperatures. The techniques include:

- open circuit potential as a function of temperature
- effective cell resistance under load as a function of temperature
- dielectric characteristics of the cell measured near room temperature ($\sim 50^\circ\text{C}$).
- DC current-voltage characteristic at reduced temperature ($\sim 400^\circ\text{C}$)
- AC complex impedance behavior of cell at reduced temperature ($\sim 400^\circ\text{C}$)
- coulometric effects on open circuit potential at reduced temperature ($\sim 400^\circ\text{C}$)

Some initial results obtained with the first three techniques are reported here.

In Figure 5. 28, the open circuit potential for an FBA cell is shown as a function of temperature, for two different fuel compositions. The cell potential is seen to fall below the theoretical values at temperatures lower than 500°C. Despite this, the cell potential responded to changes in the fuel composition down to 200°C, suggesting that diagnostic testing of the fuel electrode may be possible at these temperatures. Air electrode response to oxygen concentration will be examined in a similar manner in a future test. The origin of the open circuit potential decrease with decreasing temperature is not known at this time; it could arise from a decrease in the ionic transport number of the electrolyte, from a change in one of the electrode reaction steps, or possibly from electrical leakage in the apparatus.

Fig. 5.28—Open circuit potential vs temperature for FBA cell #3. Two different fuel compositions (10 % H_2 , 28 % H_2 , plus H_2O) were tested. Oxidant was air.

In Figure 5. 29 the effective cell resistance versus reciprocal absolute temperature is plotted. This "effective resistance" was calculated from the ratio of cell voltage to cell current, under a load sufficient to reduce the terminal voltage to one-half of the open circuit value. For comparison, the cell electrolyte resistance was calculated from the cell geometry and from published values for the resistivity of the electrolyte (yttria-doped zirconia). It may be seen that over the lower temperature range (300 to 600°C) the effective cell resistance was 200 times higher than calculated for the electrolyte alone, with a slope which was nearly the same, however. This suggests either an anomalously-high electrolyte resistivity, or some geometric factor at the electrode-electrolyte contacts (multiple point contacts). At higher temperatures the discrepancy decreases but does not disappear. We conclude that the effective cell resistance at reduced temperatures may be a useful indicator of electrolyte quality and, possibly, certain aspects of contact quality also.

Fig. 5. 29—Effective cell resistance under load vs temperature for FBA cell #3. Fuel was 10 % H_2 + 3 % H_2O in N_2 , oxidant was air.

5.2.1.5.1 Facilities for DC and AC Bench Testing of Stacks

A specialized facility has been constructed for the DC and AC bench testing of stacks. Its purpose is to provide the following information:

- overall stack performance under a variety of simulated service conditions
- important stack parameters, such as ohmic resistance and electrode diffusion factors
- safe operating limits for stack fuel, air, and electrical load parameters (to avoid irreversible electrode changes)
- new diagnostic procedures for screening out defective stacks and/or identifying specific stack defects

DC testing employs the measurement and analysis of stack current-voltage characteristics, with special attention being given to the shift in the V-I characteristic when important parameters (fuel and oxidant compositions and flow rates, stack temperature, and others) are changed incrementally.

AC testing employs the measurement of stack complex impedance as a function of frequency and the analysis of this data when plotted in the complex plane. Discussions as to how such DC and AC data may be analyzed to obtain specific polarization losses in the stack have been presented in earlier reports, and will not be reviewed at this time.

The facility can be arbitrarily divided into five systems:

- (1) stack furnace (3 zone) with associated power supply and controls
- (2) stack temperature monitoring system (digital temperature readout for up to 12 sites within the stack system)
- (3) electronic load module which can be varied manually for DC current-voltage measurements, or modulated for the AC complex impedance measurements

- (4) current, voltage, and phase measurements -- includes digital voltmeter, oscilloscope (or gain-phase meter), precision non-inductive standard resistors, and low phase-shift coupling units
- (5) fuel and oxidant gas supply systems -- includes components for the control, measurement, moisturization, and dilution of fuel and oxidant gases for the stack under test.

With this facility, DC and AC electrical testing of the stacks can be performed, as shown schematically in Figures 5.30 and 5.31. The wide variety of fuel and oxidant conditions required for the tests can be provided by the gas supply system shown schematically in Figure 5.32.

5.2.1.5.2 Verification Tests for AC Measurement System

The basic concepts of the AC measurements and the apparatus employed have been presented in previous reports and will not be repeated here. From an electrical viewpoint, a fuel cell may be described as consisting of an EMF in series with an internal resistance, or, more generally, an internal impedance. To verify correct operation of the AC measurement system, we simulated a fuel cell by setting up an EMF (a Kepco ATE-6-10M constant voltage source) in series with either known pure resistances or known R-C combinations for which the AC impedance characteristics were easily calculable. These are shown schematically in Figure 5.33.

In tests with pure resistances between 1 and 100 ohms, and at frequencies between 0.1 Hz and 50 kHz, the AC measurements indicated a constant resistive component as they should have; the indicated reactive component was negligible, as it should have been, except at the highest frequency (50 kHz), where an inductive reactance of 0.08 ohm was measured (due to inductance of the leads). This could be corrected, if desirable. For pure resistances between 100 ohms and 10 K ohms, the effects of lead capacitance become, progressively, more important: for a 10 K ohm resistance the error at 1 kHz is about 1%, but at 10 kHz it has risen

Fig. 5.30 — Typical schematic diagram for DC stack measurements. For simplicity, selector switches making the listed terminal connections are not shown

Fig. 5. 31 — Typical schematic diagram for AC stack measurements. For clarity, associated D C measurements (temperature, O_2 potential, bias current and voltage) are omitted here

Fig. 5.32 – Schematic diagram for stack gas supply system. For simplicity, details regarding regulation of the source gas systems are omitted

Fig. 5.33 — Simulated power sources with (A) purely resistive internal impedance or (B) frequency-dependent internal impedance. These were used for verification testing of the AC measurement system.

to about 15%. Note that this higher range of resistances would never arise in normal fuel cell operation; it could however become important if special diagnostic testing of fuel cells at low temperature ($<400^{\circ}\text{C}$) were shown to be desirable.

Tests with resistor-capacitor combinations were also performed. These were of importance because they provided frequency-dependent behavior in both the resistive and reactive components to be measured by the AC system. The experimental results are presented in the form of complex impedance plots in Figure 5.34 for (A) a 5 ohm resistor in parallel with a 100 μf tantalum electrolytic capacitor, and (B) a 500 ohm resistor in parallel with a 1 μf polyester film capacitor. The expected semi-circular locus with an apex frequency near 320 Hz was obtained in both cases, as one would predict. A more specific indication of good measuring ability for the AC may be seen in the "fine structure" which these two plots show. The locus for the resistor-electrolytic capacitor combination exhibited a non-zero intercept on the R-axis at high frequencies and a center of curvature lying below the R-axis; quantitatively, one can deduce that this capacitor had an effective series resistance on the order of 0.1 ohm and a power factor of about 10%, both of which are reasonable. In contrast, the locus for the resistor-polyester film capacitor combination exhibited an intercept near zero on the R-axis and a center of curvature lying on this axis; these are indicative of a relatively-low series resistance and low power factor ($<1\%$) which one would expect for this type of capacitor.

In summary, the verification tests confirmed that the AC measurement system can be used reliably for determining the impedance characteristics of an electrical power source, such as a fuel cell, over the desired range of impedance and frequency.

Fig. 5.34 — Verification tests of AC measurement system. Complex impedance behavior was measured for a constant voltage source in series with (A) a 5 ohm resistor paralleled with a 100 μ f tantalum electrolytic capacitor or (B) a 500 ohm resistor paralleled with a 1 μ f polyester film capacitor.

5.2.1.5.3 Analytical Bench Testing of Stacks

Both DC and AC analyses were conducted on series cell stack #9. This stack was used to verify AC and DC measurement techniques and provide insight into analytical techniques for data interpretation.

Analysis of DC Data, Stack #9

In a previous report⁽⁶⁾ a simple but effective theory was developed which described the V-I characteristic for a single HTSOE fuel cell with H_2 - H_2O fuel. We have used this theory to construct a computer program, STACKJ, which calculates the V-I characteristics of multi-cell stacks. This program takes into account ohmic losses, concentration polarization losses (oxygen, hydrogen, and water) and the effect of fuel composition change, as the fuel flows from cell to cell along the stack.

Predictions for the V-I characteristic from the STACKJ program were compared with experimental data for stack #9, operating under lean fuel conditions. By proper choice of the program parameters (ohmic resistance, diffusion coefficients for hydrogen and water in the porous support tube) excellent agreement with the experimental data was obtained. Two different comparisons of the experimental and calculated results are presented in Figures 5.35 and 5.36 .

In Figure 5.35, the usual voltage-current characteristic plot is used. On close examination, subtle changes in the slope of the characteristic curve may be seen which are produced by hydrogen and water mass transfer effects. The precision of our data is such that a more sensitive mode of presenting the data is needed. This can be achieved by plotting the slope, $\Delta V/\Delta I$ versus the current, I . The data is presented on this type of plot in Figure 5.36. We shall refer to $\Delta V/\Delta I$ as the "differential polarization ratio" of the stack. This will be a constant (independent of current) only when non-linear polarization effects are absent. The calculated contributions of ohmic, hydrogen mass transfer and water mass transfer processes to the differential polarization

Fig. 5.35—DC current-voltage characteristic for 9 cells of Stack # 9, operating on lean fuel (10% H₂ - 3% H₂O - 87% N₂ at 600 ml/min) and air (600 ml/min) at 1000°C

Fig. 5. 36—The differential resistance ($\Delta V/\Delta I$) versus current (I) for Stack #9, operating on lean fuel and air (same data as in Fig. 5. 35)

ratio are indicated in Figure 5.36. Experimentally, the lean-fuel operation of the stack is favorable for observing hydrogen mass transfer effects.

A valuable bonus was obtained from the STACK1 analysis of the experimental data. From this analysis, values for the effective diffusion coefficients in the porous support tube could be deduced. These values were:

$$D (\text{H}_2\text{-N}_2, 1000^\circ\text{C}, \text{porous tube}) = 0.35 \text{ cm}^2/\text{sec}$$

$$D (\text{H}_2\text{O-N}_2, 1000^\circ\text{C}, \text{porous tube}) = 0.12 \text{ cm}^2/\text{sec}$$

An independent estimate of these diffusion coefficients is available from our room temperature measurements on porous support tube $\text{O}_2\text{-N}_2$ interdiffusion, combined with high-temperature, free diffusion coefficients given in the literature. This procedure was previously described in this report. From this we obtained:

$$D (\text{H}_2\text{-N}_2, 1000^\circ\text{C}, \text{porous tube}) = 0.25 \text{ to } 0.32 \text{ cm}^2/\text{sec}$$

$$D (\text{H}_2\text{O-N}_2, 1000^\circ\text{C}, \text{porous tube}) = 0.08 \text{ to } 0.11 \text{ cm}^2/\text{sec}$$

The consistency between these two types of estimates gives us increased confidence in both the approximate values for these coefficients and the validity of the DC stack data analysis.

AC Measurements of Stack #9

AC impedance measurements were carried out on Stack #9, operating under the same fuel, oxidant, and temperature conditions as the DC measurements discussed above. The impedance of a section of nine cells in series was measured over a frequency range of 0.1 Hz to 100 kHz, superimposed on a steady DC operating current of 20 mA. A graph of the results, plotted in the complex plane, is presented in Figure 5.37. Over most of the frequency range, the data could be fitted to the equivalent circuit model shown in Figure 5.38. The circuit contains two Warburg impedance-resistor combinations: one with an apex frequency of 4 Hz, corresponding to intermediate frequency polarization behavior, and

Curve 727325-8

Fig.5.37-Complex impedance data, experimental and calculated values, for fuel cell Stack #9. Operated on lean fuel (10% H_2 - 3% H_2O - 87% N_2 at 600 ml/min) and air (600 ml/min) at 1000°C

Dwg. 7740A97

Fig.5.38—Equivalent circuit for the intermediate and high frequency polarizations of Stack #9. Z_{W1} and Z_{W2} are Warburg (diffusion-type) impedances, given in complex form by:

$$Z_{W1} = \left(\frac{85.0 \Omega}{\sqrt{f \text{ (Hz)}}} \right) (1 - j)$$

$$Z_{W2} = \left(\frac{5.94 \Omega}{\sqrt{f \text{ (Hz)}}} \right) (1 - j)$$

8

8

a second with an apec frequency of 400 Hz, corresponding to high frequency polarization behavior.

Our present hypothesis for the low and intermediate polarizations is that they are associated with water and hydrogen transport processes through the porous tube and fuel electrode. The evidence for this is as follows. The low and intermediate AC polarizations at 20 mA bias current are described by a section of the equivalent circuit (Figure 5.38) consisting of a 4.2 ohm resistance, in parallel with a Warburg impedance. This agrees well with the 4.4 ohm contribution of water and hydrogen transport to the DC differential polarization ratio data at 20 mA bias current (Figure 5.36).

The high frequency polarization has not yet been identified. It may, possibly, be associated with oxygen transport processes at the air electrode or an intergranular polarization within the solid electrolyte. By means of parameter variation (fuel composition, oxidant composition, cell temperature, bias current) it should be possible to obtain a more definite assignment of specific polarization processes to the observed AC impedance data.

5.2.1.5.4 Computer Simulation of FBA Cell Behavior

A computer program, SOLOX5, has been developed for simulating the basic electrical and chemical processes which occur in an FBA cell. In contrast with series cell stacks*, in which individual cells operate chemically and electrically in series, an FBA cell may be considered to consist of sub-cells that operate chemically in series but electrically in parallel.

Simulation of the FBA cell is more difficult than a series cell-stack; one specifies the terminal voltage of the FBA cell and from this calculates the spatial distributions of current, fuel composition and air composition. Some interesting results which have been obtained thus far are described.

- Simulative operation of an FBA cell at high fuel utilization (>90% consumption) resulted in a strong reduction in current density near the gas exit end of the cell, which automatically tended to protect the fuel electrode from oxidation in this nearly-spent fuel region. This is shown in Figure 5.39.
- The overall current-voltage characteristic for the FBA cell was similar to that for a series-cell stack (making allowances for a scale factor between currents and voltages), except when operation approached high fuel utilization. Typical characteristics for high and low fuel utilization conditions are shown in Figure 5.40. The low average current density of $\sim 260 \text{ mA/cm}^2$ at 85% fuel consumption is largely due to the high sheet resistance loss in the air electrode, which, in this study, is assumed to be $\sim 0.4\Omega$.

*Series-cell stacks have been successfully simulated with the STACK1 program, as discussed in section 5.2.1.5.3 in this report.

Fig. 5. 39—Current-voltage characteristic for an FBA cell, as predicted by computer simulation. Present state-of-the art cell parameters were assumed

Fig. 5. 40—Current density in an FBA cell as a function of position along the cell, as predicted by computer simulation. Note the protective reduction in current density near the gas exit when the fuel utilization is high.

5.2.1.5.5 Dielectric Characteristics of an FBA Fuel Cell Near Room Temperature

Dielectric measurements near room temperature are very attractive as a possible technique for testing the quality and integrity of the fuel cell electrolyte film. Near room temperature, the resistivity of yttria-stabilized zirconia becomes quite high ($\sim 10^{11}$ ohm-cm extrapolated value). As a result, an FBA fuel cell should behave very much like a ceramic capacitor, with the electrolyte film as dielectric and the fuel and air electrodes as capacitor electrodes.

To carry out such measurements with our complex impedance measurement system some minor changes were required. The function generator was used directly as an AC signal source (the electronic load modulator was removed from the circuit) and, for measuring the AC, the usual non-inductive standard resistor was replaced by a low-loss polystyrene capacitor. Our measurements enabled us to determine the AC dielectric constant, $\bar{\epsilon}$, which in complex form may be written as $\bar{\epsilon} = \epsilon' - j\epsilon''$. The real component, ϵ' , approaches the static DC dielectric constant at low frequencies, while the imaginary component, ϵ'' , is strongly influenced by AC dielectric losses in the material. A more common measure of dielectric loss is the dissipation factor, D , which is just the ratio of ϵ'' to ϵ' .

Our measurements were performed on FBA cell #3 at 44°C, over a frequency range of 10 Hz to 100 kHz. The results are plotted in Figure 5.41. The real part of the dielectric constant varied from 21 to 10, whereas literature values for stabilized zirconia have been reported to be approximately 26, and nearly independent of frequency over this range. Also the dissipation factor, D , was nearly constant but rather high (about 0.13), compared to the values usually obtained with ceramic materials (about 0.01 or less). The observed behavior might arise from defects within the electrolyte (inhomogeneity, grain boundaries) or from an interfacial layer which is partially conducting and which has different dielectric properties.

Further measurements at slightly higher temperatures (up to 200°C) may aid in interpreting the results, especially, if a loss peak

Fig. 5.41—Dielectric parameters vs. frequency for FBA cell #3 at 44°C. These parameters correspond to the cell electrolyte film which becomes semi-insulating at room temperature.

in ϵ'' versus frequency is observable. Even if the data do not yield a simple interpretation, the magnitudes and frequency dependence of ϵ' and ϵ'' may be found to correlate with electrolyte film quality and composition.

5.2.1.5.6 Analysis of AC Data, FBA Cell #3

The complex impedance of FBA Cell #3 was measured at 800°C*, over a frequency range of 0.1 Hz to 50 kHz, superimposed on a DC bias current of 200 mA. Fuel and oxidant mixtures were the same as in the previous DC measurements. The data, plotted in Figure 5.42, are qualitatively similar to the results for Stack #9 (discussed earlier in Section 5.2.1.5.3). Two major arcs are evident which may correspond to two distinct diffusion-like polarization mechanisms. The apex frequencies are at least one order of magnitude lower for this cell, compared to those for Stack #9; this is probably the result of the lower temperature employed in the FBA cell measurements.

Assignment of specific mechanisms to the two polarizations observed is not possible with the data available thus far. One may speculate, however, that the lower frequency polarization might once again involve water transport at the fuel electrode, since this appears to be a prominent component in the DC differential polarization ratio.

*At 1000°C, inductance corrections for an FBA cell are relatively quite large, due to the very low cell resistance; consequently, 800°C was chosen for the measurements here. Improvements in our measurement technique should make it possible to obtain reliable AC data at 1000°C.

Fig. 5.42—Complex impedance data for FBA cell #3, operating at 800°C on lean fuel (10% H₂ - 3% H₂O - 87% N₂) and air, both at 600 ml/min. Bias current was 200 mA

5.2.1.5.7 Analysis of DC Data, FBA Cell #3

Initial DC testing of FBA cell #3 was performed at 800°C, with a fuel mixture of 10% H_2 -90% N_2 with 3% H_2O , and air as oxidant. The current-voltage characteristic and the corresponding differential polarization ratio plot are presented in Figures 5.43 and 5.44. The principal feature visible in the differential polarization ratio plot is a large component of water vapor transport polarization. The remainder of the polarization ratio is believed to consist of a large ohmic component plus a component due to oxygen transport polarization in the air electrode. The latter two contributions are constant at the low current densities achievable with the cell at 800°C and hence could not be separated as they were for the data of Stack #9. The origin of the high water vapor polarization component is puzzling. Localized contact sites between the fuel electrode and electrolyte could produce such an effect and, in addition, would give rise to a high ohmic resistance which may be present here. The situation should be clarified by future DC data taken at 1000°C with low fuel and oxygen supply concentrations.

5.2.1.5.8 Analysis of the Current Distribution in the Interconnection and Electrolyte Layers

For simplicity it is usually assumed in thin film fuel cell analyses that the current flow is uniform through the interconnection and electrolyte films. In certain instances, however, it can be quite non-uniform, which will have important consequences, regarding resistance, heat dissipation, and concentration polarization. The non-uniformity becomes pronounced when the lateral resistance of either electrode exceeds twice the perpendicular resistance of the interconnection (or electrolyte) film. Current flow then tends to concentrate near the ends of the interconnection region, or very strongly near one end if one electrode has a significantly lower resistance than the other electrode.

In most cases this current flow problem can be reduced by changing the lengths, the thicknesses, or the resistivities of the films. To study this problem of current non-uniformity and to determine the effectiveness of film parameter changes in reducing it, we employed a

Fig. 5.43—DC current voltage characteristic for FBA cell #3, operating at 800°C on lean fuel (10% H₂—3% H₂O—87% N₂) and air, both at 600 ml/min

Fig. 5.44—Differential polarization ratio vs. current for FBA cell #3, operating at 800°C , on lean fuel and air (same data as Figure 5.43).

finite-element model to simulate current flow in interconnection and electrolyte films. This is pictured in Figure 5.45. The simulation analysis is carried out by a computer program, FINELL, with provisions made for varying the number of finite elements and the values of the film parameters. Special options may be introduced into this program, such as the simulation of extended surface contacts, and the simulation of films having a tapered thickness.

As an initial problem, we considered the interconnection system shown in Figure 5.45A with the following parameters:

Interconnection length, $l = 0.75$ cm

Interconnection width, $w = 1$ cm

Interconnection resistivity-thickness product = 0.02 ohm cm^2

Fuel electrode sheet resistance = 0.1 ohm

Air electrode sheet resistance = 0.4 ohm

We wished to determine the current density profile through the interconnection, and also, to determine what effect doubling, or quadrupling, the air electrode thickness would have on this profile. The results are presented in Figure 5.46. It can be seen that quadrupling the air electrode thickness reduced the current density non-uniformity to an acceptable level; also, it decreased the overall resistance of the interconnection system by 38%. A second means for reducing current non-uniformity is to increase the thickness of the interconnection film itself. The results, which will not be presented here, showed that this approach was much less effective and, in addition, increased the overall resistance of the interconnection system considerably.

Other variations on this problem will be tested in the future, as the need arises.

(A)

(B)

Fig. 5. 45— Schematic of an air electrode-interconnection-fuel electrode system (A) and the finite element analog to the system (B)

Fig. 5.46 — Relative current density vs position along the interconnection for the system shown in Figure 5.45A. Values were calculated using the analog shown in Figure 5.45B.

6.0 FUTURE WORK

1. Support tube work will be aimed at producing quality closed-end tubes, by various end closure schemes, to closer dimensional tolerances.
2. Air electrode work will be aimed at identifying the best candidate for the FBA cell, i.e., having the best combination of thermal expansion, electrical conductivity, fabricability and stability, when operating in the fuel cell at 1000°C.
3. FBA cell work will be aimed at improving the cell performance by reducing total cell resistance, especially at the air electrode/electrolyte interface. Also work on the FBA cell will be aimed at demonstrating long-time life stability under anticipated operating conditions.
4. Mock-up tests will be designed whereby the HTSOE fuel cell module (the generator building block) design will be preliminarily evaluated to establish that the design is both feasible and workable, with respect to its more critical elements of construction and operation.
5. Analytical testing of cell components and cells will continue.
 - a) Porous support tube, gas transport properties:

Diffusion tests will be continued on porous tubes, including some tubes which are coated with the porous air electrodes. Comparison tests of O_2-N_2 and O_2-He diffusion will be used to check on the importance of Knudsen diffusion in the pores.

- b) DC and AC testing and analysis:

DC and AC tests will continue with emphasis being placed on determining ohmic resistances of individual cell components: inter-connection, air electrode, fuel electrode, and electrolyte. Electrode behavior at very low fuel and air concentrations will receive increased attention.

c) Diagnostic testing at reduced temperatures:

Previously described diagnostic tests at reduced temperature will be continued to determine which of them are practical, sensitive indicators of cell performance at normal operating temperatures.

d) Computer analysis of cells:

Emphasis will be placed on comparison of experimental and simulation results under low fuel and air concentration conditions, in order to obtain numerical estimates of important cell parameters, such as the ohmic resistance, the air electrode diffusion factor, and the fuel electrode diffusion factor.

7.0 REFERENCES

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8.0 APPENDIX A

OPERATION, DESIGN CONCEPT AND APPLICATION OF THE HIGH-TEMPERATURE, SOLID OXIDE ELECTROLYTE FUEL CELL

A.1 INTRODUCTION

Fuel cells are electrochemical generators of direct current electricity. Unlike conventional generators, based on heat cycles, they have no Carnot efficiency limitations, and can, theoretically, yield high energy efficiencies. Of all fuel cell power systems, that system, based on a stabilized-zirconia solid electrolyte, offers the highest achievable efficiency. A recent design study indicates that power densities of $\sim 3 \text{ kW/ft}^3$ of fuel cell/high-temperature heat exchanger assembly can be achieved with state-of-the-art materials and fabrication processes. The high-temperature, solid oxide electrolyte (HTSOE) fuel cell would operate at 1000°C , without the need of expensive catalysts, on a carbon monoxide-hydrogen gas mixture, provided by the gasification of coal. The fuel cell generator would operate at 1000°C for several reasons: a) the resistivity of the solid electrolyte is sufficiently low at this temperature to permit high levels of electrical efficiency at high current densities, and b) the high-grade heat released can be used for steam generation, which can be used for steam bottoming, to increase overall fuel heat content utilization, or for direct sale.

In one concept, clean pipeline coal gas could be supplied to the high-temperature, solid oxide electrolyte fuel cell and the by-product, hot exhaust gas (CO_2) from the fuel cell generator would be used to produce steam in an off-gas, waste heat boiler. This steam would then be used to support either an industrial process, adjoining the fuel cell site, or for additional power generation, via a steam turbine, or both, to enhance the overall system efficiency.

Apart from the efficiency advantage and the use of a noncritical fuel, the HTSOE fuel cell is attractive from other standpoints.

- Air pollution from the fuel cell power system would be minimal. (Carbon dioxide and water vapor are the only species emitted).
- Since the heat rejected by the fuel cell could be employed to produce process steam, thermal pollution of the environment, due to waste heat, would be minimized.
- The fuel cell generating process would not require cooling water, consequently, siting of plants would not be dependent on plentiful water supplies.

The commercial feasibility of this new power system greatly depends on the useful life of the generator. At the onset of the present program, the thin-film cell stack had achieved ~5000 hours at temperature, under a variety of fuel conditions, and eleven thermal cycles, but with the promise of much longer life indicated by the stable nature and makeup the individual component layers of the fuel cell itself. The ERDA-directed, NASA-managed, Energy Conversion Alternatives Study, conducted in 1975-76 at the Westinghouse Research Laboratories, indicated that, for fuel-cell power systems to be competitive from an electricity-cost standpoint, the useful life of the fuel cell module must exceed 30,000 hours. A recently completed study indicated the benefit of the HTSOE fuel cell generator in an industrial cogeneration application (an integrated aluminum plant)

A.2 TECHNICAL BACKGROUND

Solid electrolyte fuel cells generate electrical energy from fuel and air. In this section a fuel cell power system is described, including: how solid-electrolyte cells produce electrical energy, how individual cells can be combined to form high-performance modules which can be combined to produce a generator, and how the generator can be combined with auxiliary equipment into a plant concept. Also reviewed.

are the major technical problems that must be resolved to allow demonstration of a long-lived, high-performance fuel-cell battery.

A.2.1 How Solid Electrolyte Fuel Cells Generate Electricity

As shown in Fig. A.1, a solid electrolyte fuel cell consists of four basic components: an air electrode, a solid electrolyte, a fuel electrode, and a porous support tube. A fifth component, the interconnection between adjacent cells, is not shown. The porous tube of stabilized zirconia, which serves as a mechanical support for the fuel cell, has an approximate wall thickness of 1000 μm .

Exposed to the air flow is the air electrode. One kind is a conducting oxide current collector, tin-doped indium oxide, fabricated in a porous structure that is readily permeated by oxygen from air which flows over it. Here, praseodymium oxide is discontinuously deposited onto this current collector and represents the active part of the air electrode. This active PrO_2 effects the necessary $\text{O}_{2(g)}$ to $2\text{O}^=$ transition. Oxygen molecules from the air accept electrons through an external electronic circuit, leaving the electrode positively charged, and forming oxygen ions $\text{O}^=$, as shown in Fig. A.2.

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Fig. A.1 Schematic Cross-Section of a Thin-Film Fuel Cell

- 1 Oxygen molecule diffuses through air to electrode
- 2 Oxygen atom picks up two electrons from air electrode to form oxygen ion in electrolyte
- 3 O^- oxygen ion transport through electrolyte
- 4 Fuel diffuses to reaction site and reacts with O^- ion releasing electrons to fuel electrode
- 5 Reaction product leaves reaction site
- 6 Electrons from fuel electrode flow through external load to air electrode

Fig. A.2 Schematic Diagram of a Solid Electrolyte Fuel Cell, Indicating How Oxidation of the Fuel Generates Electric Current to the External Load

If the external circuit is closed, the oxygen ions enter the second component of the cell, a dense zirconia ceramic, such as yttria-stabilized zirconia (solid electrolyte) and pass through this layer at elevated temperature, due to the oxygen concentration gradient across the ceramic.* If an $O^{=}$ enters at the air electrode-electrolyte interface, an $O^{=}$ emerges at the electrolyte-fuel electrode interface, thus preserving the electrical neutrality of the material. The gases on either side of the cell will not penetrate through this impervious electrolyte layer, so that the reaction can only take place when current is drawn from the cell stack. Since the ceramic electrolyte has no electronic conductivity, no electrical short circuit can occur in the cell.

Exposed to the fuel flow in the figure is the fuel electrode. The porous fuel electrode is a nickel-zirconia cermet. At the fuel electrode the fuel gases, CO and/or H_2 react with the emerging $O^{=}$ ions to form reaction products CO_2 and/or H_2O . Electrons emerge from the fuel electrode. In this way the fuel electrode becomes negatively charged.

These three layers -- an electrolyte sandwiched between two electrodes -- constitute a single solid electrolyte fuel cell.

The voltage developed between the electrodes of the cell is a function of the oxygen partial pressure gradient between air and the fuel gas. When current is drawn, the cell voltage lies, typically, between 0.95 and 0.65 volt.

Electrical energy and power is delivered by the cell when a load is connected between the two electrodes. Electrons will then flow from the negative fuel electrode to the positive air electrode through the load circuit. Current can be drawn from a cell, as long as air and fuel gases are supplied and the combustion products removed. The output voltage produced at such currents is a function of the ohmic losses and concentration polarization losses in the electrodes.

*This gradient is established with air on one side and fuel gas on the other side.

A.2.2 Operation of the High-Temperature Fuel Cell

To produce a practical energy system, individual cells must be assembled in such a way as to generate large voltages and sizable quantities of power.

Therefore, the basic solid electrolyte fuel cell system would include a fuel cell generator, a ceramic heat exchanger and an inverter (DC or AC). Coal-derived fuel gas (a CO and H₂ fuel gas mixture) is fed to the fuel cell generator, which has been treated to remove particulate material and excess sulfur compounds. In the generator, the fuel gases are electrochemically oxidized to CO₂ and H₂O.

The fuel cell generator will operate at ~1000°C for the following reasons: (a) the resistivity of the solid electrolyte is sufficiently low (~20 Ω cm) to permit high levels of electrical efficiency at high current densities, (b) the heat released in the fuel oxidation can be efficiently used elsewhere.

The air necessary for the operation of the generator is brought in separately. The N₂ of the air and the unreacted O₂ emerge from the generator, exchange heat with the incoming air, and exhaust to the surroundings. AC power can be available by using a DC converter network.

A.2.3.1 The Fuel Cell-Heat Exchanger System

Figure A.3 indicates the components of a possible HTSOE fuel cell generator-heat exchanger system. Here the fuel cell generator would be composed of a high-temperature, heat exchanger component that is integrated with the cell stacks. The system would allow preheating of air in a ceramic heat exchanger to the operating temperature of the cell stacks. Fuel could be preheated in heat exchanger, external to the generator, using off-gas from the fuel cells or be preheated within a preheat section of the generator. A ceramic heat exchanger is necessary because of the unavailability of metallic alloys that are stable at up to 1000°C for extended periods of time.

Fig. A.3 - Heat exchange - generator - power conditioning scheme

A.2.3 High-Temperature, Industrial Cogeneration Systems

A potential application for the HTSOE fuel cell would be in an industrial cogeneration plant. Such a plant would be capable of delivering steam from an off-gas, waste heat boiler to an industrial process, or for power generation (by a steam turbine), or both.

A.2.4 Fuel Cell Industrial Cogeneration

For the cogeneration scheme the fuel cell auxiliary systems components and their flow diagram interrelationships are given in Fig. A.4. The coal gas supply system (not shown) would deliver clean, pipeline coal gas to the cogeneration system. Salient features of this system would include the following:

1. Coal gas would arrive from some central gasification facility, would be distributed to the industrial site at an intermediate BTU value, and would be delivered at 1 bar, with no more than 100 ppmv H_2S , with provision for additional desulfurization, if needed.
2. Products of combustion from the gas would contain less than 0.1 lb. $SO_2/10^6$ Btu to meet any SO_2 control level now in existence, or proposed.
3. Fuel and air preheaters would use 800°C gas from the fuel cell outlet combustors.
4. Start-up heat would be supplied at 900°C for a limited period of time, to provide start-up fuel and air at 800°C to the fuel cells. These conditions represent the maximum temperatures that would be achieved in the heat exchanger (only during the last few hours of cell start-up heating).
5. Preheater materials and design would consider the presence of H_2S in the fuel gas to avoid carbon deposition from a reverse Boudouard reaction.
6. Steam from the off-gas waste heat boiler would be used by an industrial process, adjacent to the fuel cell site, or for power generation, or both.

Fig. A.4 - Proposed HTSOE fuel cell auxiliary systems