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GENERATING SYSTEM

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MASTER

Second Quarter Report
Covering the Period
July 1, 1978 to September 30, 1978

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A. O. Isenberg, Technical Coordinator
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by

Research and Development Center
WESTINGHOUSE ELECTRIC CORPORATION
Pittsburgh, Pennsylvania 15235

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1.0 ABSTRACT

1. Oxygen loss behavior in the lanthanum chromite interconnection material was investigated by the microweighing technique. Oxygen losses were only slight up to 10^{-8} atmospheres of oxygen partial pressure, increasing to 0.32% of total oxygen content at 10^{-16} atmospheres of oxygen at 1000°C (using a water/hydrogen mixture). Oxygen loss of this amount did not seriously hamper electrical conductivity of the interconnection.
2. RF sputtered interconnection bands have been produced that display suitable density to permit the technique to be used in the construction of cell stacks.
3. Electrochemical vapor deposition equipment has been modified to enable preparation of 20 cell fuel cell stack fabrication to proceed. The equipment is being used in preliminary runs to establish suitable conditions for proper lanthanum chromite film deposition. Then experiments are aimed at depositing the desired magnesium-aluminum doped lanthanum chromite composition.
4. The fuel electrode process and equipment have been improved to permit fabrication of long (0.3 m) tube segments, showing good mechanical and electrical properties.
5. Long tube sections have been used to fabricate air electrodes, having desired porosity without loss of conductivity. Here, the seeding technique, described in the Final Report of the initial contract, has been used.
6. Porous support tube work (involving equipment and fabrication techniques) is being extended to the fabrication of 0.3 m long tubes, needed for the fabrication of the 20 cell stacks.

7. Work continues on the construction of the 5 station fuel cell stack life test facility. The fully instrumented facility will be completed and ready for testing by the end of this calendar year.
8. Theoretical interpretations of fuel cell stack polarization losses have been compared with actual measured losses in the 5 cell fuel cell stack that was previously tested in the program. Good agreement between predicted and actual results was obtained. The analysis has suggested a nondestructive, diagnostic DC measurement technique for determining overpotential contributions from both the air and the fuel electrodes of a fuel cell stack. The technique utilizes constant current and two (or more) levels of fuel concentration and oxygen partial pressures in air.
9. An analyses of the intercell leakage current in the five cell fuel cell stack that was life tested for 700 hours was conducted. The fuel electrode preparation introduced an intercell leakage current that caused about 3-4% reduction in open current potential, below theoretical.

2.0 PREFACE

For those who are unfamiliar with the objectives and results obtained during the first 2 year contract period of this program, a Past Program Summary is given in Appendix A.

For purposes of providing background information to those readers who may be unfamiliar with the operation, design concept and application principles of the high-temperature, solid oxide electrolyte (HTSOE) fuel cell, Sections B1 and B2 have been included in Appendix B of this report.

3.0 INTRODUCTION

This report constitutes the second quarterly report, under DOE continuation Contract No. EY-76-C-03-1197. This report presents progress on work, acutally building on and continuing from the level of technology attained on the HTSOE fuel cell during the initial 2-year phase for DOE, that ended on March 31, 1978.

4.0 THE PRESENT PROGRAM

The present two-year research program (DOE Continuation Contract EY-76-C-03-1197), relating to the development of the high-temperature solid oxide electrolyte (HTSOE) fuel cell is building upon the findings of the first 2 year contract effort at Westinghouse.⁽¹⁾ It will demonstrate extended performance and life stability of thin film, HTSOE fuel cell stacks. The fuel cell stack, a multiplicity of series-connected cells, constitutes the basic building block of this fuel cell system. These stacks are being constructed, using the component materials and their fabrication processes developed in the past program, and those materials and processes that are being further optimized during the first year of this program. Extended life will be demonstrated in single cells and small cell stacks, under conditions anticipated in the operation of stacks in a total fuel cell system. Other stacks will be tested to determine power output capability and the effect of fuel/air conditions on performance. Also, the reproducibility of stacks, with respect to cell-to-cell and overall performance, will be demonstrated, with at least 10 stacks constructed and evaluated for that purpose.

During the proposed program, four milestones will have been attained. For Milestone $\nabla 1$ all the five fuel cell components -- porous support tube, fuel electrode, solid electrolyte, air electrode and the interconnection -- will have been specified and the fabrication sequencing and fabrication techniques will have been established in a "benchmark" stack, delivering 10W of power. To attain Milestone $\nabla 2$ at least a single cell, including an interconnection, will have demonstrated a minimum of 1000 hours of life at 1000°C, under the following conditions:

- Current density of 400 mA/cm²

- Voltage stability - No more than 10 percent degradation from the initial operating cell voltage in a $H_2 + 3\% H_2O$ inlet fuel mixture.

Attainment of Milestone $\nabla 2$ will show that the thin film, high-temperature fuel cell concept and design is viable and should show promise of further life improvement toward what is required for utility central station operation. Achieving Milestone $\nabla 3$ will require that a small fuel cell stack, having at least 20 series-connected cells, demonstrate a minimum of 1000 hours of operation, under the same conditions as for Milestone $\nabla 2$. Milestone $\nabla 4$ will be attained when 10 stacks will have been fabricated and tested, for a short time, to demonstrate reproducibility in materials fabrication and uniformity in cell and stack performance. The same test conditions as described for the other milestones will be used to operate the 10W stacks.

Therefore, the program will evaluate the components and verify the fabrication techniques developed to produce them. It will establish the ability of these components to operate properly in contact with each other in the thin film design under simulated service conditions. Also it will determine the long-time stability characteristics both of the components and their interfaces and of cell and cell stacks under simulated service conditions.

Finally, sufficient cell stacks will be fabricated to verify their reproducibility, performance and life. With these objectives attained, the basic building block of the HTSOE fuel cell generator will have been firmly established.

Upon achievement of the milestones of this proposed program, the high-temperature, solid oxide fuel cell development program will then be advanced to the stage of system design, prototype construction and testing.

5.0 OVERALL TECHNICAL EFFORT

The overall technical effort is aimed at achieving four milestones in the 2 year period of the contract. These include:

- 1) specifying all five fuel cell components, their fabrication sequencing and their fabrication techniques in a "bench mark" stack, delivering 10 watts of power;
- 2) demonstrate, at least in a single cell with an interconnection, a minimum of 1000 hours of life at 1000°C, under the conditions of 400 mA/cm², no more than 10 percent voltage degradation from initial loaded voltage, using H₂/3% H₂O inlet fuel mixture;
- 3) demonstrate 2) in a fuel cell stack of at least 20 series connected cells;
- 4) fabricate and test, for a sufficient time, 10 stacks to demonstrate reproducibility in materials fabrication and uniformity incell and stack performance.

5.1 TASK 1. DEVELOPMENT AND REFINEMENT OF FABRICATION PROCESSES

Work in the task includes:

- 1) fabrication of the cell interconnection by the EVD process
- 2) definition of the fuel electrode stack process
- 3) definition of the air electrode stack process
- 4) porous support tube refinement
- 5) cell stack preparation.

5.1.1 Subtask A. Interconnection Fabrication

Work in this quarter on the interconnection concentrated on understanding oxygen-loss behavior mechanisms and their effect(s) on physical properties, as electrical resistivity, and refinement of the EVD process to

produce properly-doped lanthanum chromite inter-connection films. Inter-connection films were prepared by RF sputtering for basic property evaluations.

5.1.1.1 Lanthanum Chromite Interconnection

Lanthanum chromite, doped with magnesium ion, has the basic requirements for use as an interconnection in the thin layer high temperature fuel cell. This is evidenced by physical and chemical properties of the bulk oxide and its successful operation in a test fuel cell stack.⁽¹⁾

In the previous quarterly report on this contract⁽²⁾ we described measurements of oxygen loss from bulk specimens of pure and magnesium-doped lanthanum chromite as a function of oxygen partial pressure. It was found that in some instances lanthanum chromites, prepared and heat treated between room temperature and 1000°C, were formed in a metastable and perhaps nonstoichiometric form which exhibited larger oxygen losses at comparable oxygen partial pressures than materials of similar composition which had been prepared at much higher temperatures (1650-1700°C). Larger oxygen losses of this type lead to larger oxygen vacancy content, which may increase unwanted oxygen diffusion through an interconnection of such an oxide.

It is thus desirable to examine the oxygen loss behavior of an actual lanthanum chromite interconnection film, stripped from the nickel electrode of a fuel cell stack. Although the lanthanum chromite interconnection films are normally very adherent, in one instance a $\text{LaCr}_{.965}\text{Mg}_{.035}\text{O}_3$ interconnection was prepared without the Al^{3+} additive required to give a good thermal expansion match, and it was possible to strip this film directly from the nickel cermet fuel electrode. This film showed the expected orthorhombic crystal symmetry by X-ray diffraction and a high (99.5% of theoretical) density. Chemical analysis of both film surfaces and a fracture edge by the EDAX technique (Energy Dispersive Analyzer X-ray) and analysis for magnesium and aluminum by the atomic absorption method showed that the film was lanthanum chromite doped by magnesium to the extent indicated by the formula $\text{LaCr}_{.965}\text{Mg}_{.035}\text{O}_3$.

Weight change measurements in a controlled atmosphere high temperature microweighing system are shown in Figure 5.1. The data indicate that the oxide loses only a slight amount of oxygen up to 10^{-8} atmospheres oxygen partial pressure. This increases to about 0.32% of the total oxygen content at 10^{-16} atmospheres oxygen (using a water/hydrogen mixture), as measured by a zirconia electrolyte oxygen gauge next to the sample at 1000°C.

Assuming that one positive hole charge carrier is present for each Mg^{2+} , these data suggest that at 10^{-16} atmospheres oxygen pressure, 55% of the positive hole charge carriers are lost to provide charge compensation for the oxygen ions removed from the magnesium-doped lanthanum chromite. This would be expected to reduce the conductivity, as would positive hole trapping and charge scattering effects resulting from additional crystal structure imperfections. Earlier conductivity measurements⁽¹⁾ of sputtered films of $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$ showed factors of six to ten drop in resistivity between air and water hydrogen (10^{-15} - 10^{-16} atmospheres O_2 pressure) atmospheres.

Provided no high interface resistances are encountered, the conductivity values anticipated for the interconnection from these results are well within the useful range for the fuel cell stack.

5.1.1.2 Radio Frequency (RF) Sputtering of Interconnection Material

Ni-Cermet coated porous support tubes were heated and rotated during the deposition of $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$ thick films. To rotate the tubes during deposition a 2 mil support sleeve of molybdenum metal was placed on the inside of the tube. This sleeve was attached to a drive shaft which was connected via a flexible cable and feed-through to a speed controllable motor. Inside the molybdenum sleeve was stationary a cartridge heater. During a 43 hour run the outside flexible cable broke, due to excessive stress, from which time on, the tube was rotated by hand 180° then 90° and then repeated for a total time of 216 hours. Also the diffusion pump failed after 168 hours so that this run (Z9-77) was considered inferior.

Fig. 5.1 - Oxygen loss from $\text{La Cr}_{.965}\text{Mg}_{.035}\text{O}_3$ interconnection layer stripped from nickel cermet fuel electrode

The cross-section of the coated sample of Run Z9-77 is shown in Figure 5.2. Note the irregularity of the film. The thickness of the $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$ sputtered layer was measured microscopically and the porosity of the film was studied.

The zirconia tube when covered with the fired Ni-Cermet electrode, is very porous. It is difficult to coat this porosity with a dense interconnection layer. To overcome this obstacle for dense films, a slurry of yttria stabilized zirconia powder was rubbed into the tube's surface irregularities and then the interconnection material was sputtered onto the preconditioned tube (Run Z10-87).

The potted and polished cross sections of this run are shown in Figure 5.3. One observes some crack like features in the film and one observes the rings, created by the intermittent rotation of the tube during sputtering. During this run, an automatic timer activated the motor for rotating the substrate tube. The tube was turned about 100 degrees every hour. The interconnection film appeared to be smooth and had good coverage over the filled holes of the fuel electrode. To test gas tightness, the ends of the tube was closed and vacuum was applied. The film showed (for the first time), that considerable improvement in film density was achieved by RF sputtering.

Left

Center

Right

Fig. 5.2 Cross section of Run Z9-77 showing the sputtered $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$ layer on the nickel-cermet fuel electrode.

During previous experiments, all LaCrO_3 targets were bonded to the RF electrode. Through heating and cooling the target cracked. The targets had been made by an outside vendor and the target density was low so that its mechanical strength was insufficient. Therefore, a graphite die was built and a new target was hot pressed, in house, from purchased powder. The set-up shown in Figure 5.4 was used in the hot pressing of the 4" diameter x 1/4" thick target to a density of nearly 97%. A radio frequency heater was used to heat the die and powder in a nitrogen atmosphere. Only graphite was used to hold the powder charge. A 2-1/2" diameter hydraulic press was used to apply the necessary pressure. The maximum pressure was applied at room temperature, then the temperature was raised. The optimum pressure and temperature for fabricating the $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$ target is 3000 psi and 1650°C. Pressing

Left
54.4 μ thick

Center
89.1 μ thick

Right
107.0 μ thick

Fig. 5.3 Cross section of Run 10-87 nickel-cermet coated fuel electrode with surface pores filled with a slurry of yttria-stabilized zirconia and $\text{La}_{.98}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$ sputtered on the outside.

Figure 5.4. Hot-Pressing Apparatus for Fabricating Interconnection Materials (N_2 Atmosphere, Target: 4" diameter x 1/4" Thick)

time at maximum temperature was 2-3 hours.* After hot pressing, the target was ground to remove any undesirable surface materials, due to the contact with graphite at elevated temperatures.

The sputtering system was cleaned and reassembled with the in house hot pressed $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$ target. A 5 mil indium foil disc was placed between the target and the RF electrode to enhance the electrical contact.

Run Z11 was made to clean the new target. A thermocouple was wrapped around the cartridge heater to monitor the temperature. After this run the La CrO_3 target looked very smooth and clean.

Run Z12-70 was used to experiment with methods of band masking. First the Ni-Cermet fuel electrode was coated with aluminum foil, exposing the area on the tube to be coated with the interconnection material. These bands were spaced as shown in Figure 5.5 (bottom). The $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$ films have a smooth and dense appearance. Figure 5.5 (top) shows the substrate arrangement with rotating shaft, heater and target.

Preparations are being made to sputter $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$ as interconnection bands on a Ni-Cermet fuel electrode for stack fabrication.

Conclusions:

Progress has been made in the fabrication of sufficiently dense layers of modified lanthanum chromite. Also masking techniques have been identified to achieve interconnection bands. The next step is the incorporation of sputtered interconnection bands into a working cell stack of at least three cells to enable test evaluation of such interconnection films.

5.1.1.3 Electrochemical Vapor Deposition (EVD) Material Preparation

Two of the halide delivery source materials needed in the EVD deposition process; La O Cl for the interconnection and yttria-stabilized

*This work was done by C. A. Anderson, J. A. Kuszyk and W. J. Carmen of the Westinghouse Research Laboratories.

Fig. 5.5a Arrangement of substrate and heater over target in R. F. Sputtering System

Fig. 5.5b Sputtered interconnection layer over Ni-cermet fuel electrode

zirconia for the electrolyte, had to be prepared before further battery stack fabrication could take place. To prepare the materials, the respective compounds are ball milled with carbon, an organic binder, and a suitable solvent. Intimate contact with the carbon is required, since carbon plays an important part in the chlorination reactions that take place during deposition experiments, as seen in equations (1) and (2):

The organic binder gives strength to the dried material. To assure immediate delivery of the chlorides, all the material is prechlorinated in small batches. Sufficient quantities of these materials are now available for continued stack fabrication.

5.1.1.4 EVD Apparatus Improvement

Three improvements on the EVD deposition apparatus have been implemented.

- 1) An oxygen gauge has been installed for monitoring the hydrogen-water vapor mixture on the substrate inside to prevent nickel oxidation.
- 2) An improved gas valving the safety shut-off system for carrier and reaction gases has been constructed.
- 3) Graphite cartridges that contain the source materials for the halide vapor delivery have been redesigned.

The oxygen gauge has been added to monitor the oxygen activity of the fuel electrode protection gas. A sensing circuit has been designed and built that follows the oxygen gauge output. Should the gauge output drop below an adjustable set-point, the instrument activates a solenoid valve that shuts off all gas to the partially-fabricated battery stack. This action prevents damage to the fuel electrode that would occur if an oxidizing atmosphere were injected. Once reducing conditions have been restored, normal operation is resumed.

An all new gas valving system has been installed on the EVD apparatus that will reduce the possibilities of leaks and increase reproducibility in deposited films. The new system, made entirely of glass and teflon tubing, minimizes the chances of leaks, associated with the corrosion of standard fittings. The majority of connections are now ground glass joints. All carrier gases and non-corrosive gases have been "hard" plumbed in and pressure tested for leaks.

The graphite delivery cartridges used in the deposition of inter-connection material have been re-designed with emphasis placed on symmetry and purity of deposited films. Figure 5.6 shows two of the new cartridges. The upper one is an assembled cartridge that has been used in several deposition experiments. It is a three chambered design and permits deposition of a three component system. The lower cartridge is four chambered and shows in exploded form the internal design and associated pieces. Spring loaded pistons in each chamber help to maintain uniformly packed beds of reactants during the duration of the deposition process. Replacement parts are available for all cartridges.

5.1.1.5 Electrochemical Vapor Deposition of Modified Lanthanum Chromite

Besides introduction of safety and reliability features to the EVD process as described in Section 5.1.1.4, we are in the process of developing an alumina-doping scheme for modified lanthanum chromite. Alumina addition of nearly 25 mol % is the goal of this work. The preferred occlusion of aluminum in the lanthanum chromite was detected earlier by analysis of the film material. This came as a surprise and was explained as stemming from alumina reactor components.

Four deposition runs have been made to date, that had controlled alumina doping as the end-goal. All four runs resulted in undesirable, multiphase coatings of unknown deposition. A qualitative flame spectrometric analysis of one film revealed an excessively high content of aluminum. This is not surprising because the previous involuntary alumina doping already lead to a coating containing nearly 15 mol % aluminum. It is expected that approximately ten more coating experiments are required

Fig. 5.6 Graphite delivery cartridges used in the
deposition of interconnection material.

in order to establish EVD conditions that produce the proper alumina level in the modified lanthanum chromite coatings, before a 10 watt stack can be constructed with the proper composition of interconnection material.

5.1.2 Subtask B. Fuel Electrode Stack Process

The fuel electrode stack process is being expanded to enable fabrication of larger fuel cell stacks, of 20 cells, or more, without loss of performance.

5.1.2.1 Furnace Fabrication

Target fuel cell stacks will consist of a minimum of twenty series-connected cells that can deliver 10 watt DC electrical power. The 20 cell stack requires the fabrication of longer fuel electrodes of nearly 0.3 m (~1 ft) in length.

Existing sintering furnaces did not allow the fabrication of such fuel electrodes because of limitations in length, heating rate, vertical mounting, and temperature level. It was not possible to locate a supplier to fabricate a furnace in a reasonable time span and of an acceptable price to satisfy program requirements. Required furnace characteristics are: an average heating rate of 60°C per minute up to 1700°C; vertical mounting, to prevent sagging of stack tubes, a uniform temperature zone of nearly 0.3 m.

A tube furnace, that satisfies all requirements mentioned above has been engineered, constructed and tested in-house, and long fuel electrodes can now be sintered routinely in this furnace. The furnace is operated with a molybdenum heating element which is protected by a forming gas atmosphere. The insulation consists of an alumina fiber mat (SAFFIL) and the tube material is high purity alumina.

5.1.2.2 Fuel Electrode Sintering

Fuel electrodes are prepared by the standard technique that involves dipping of the porous support tube into a nickel oxide/zirconia slurry, drying, sintering in an oxygen containing atmosphere, cooling below the melting point of nickel, and, finally, reducing the nickel

oxide to nickel. The mechanical integrity of the fuel electrode can be enhanced by sintering at high temperatures. Long time exposure of nickel oxide to stabilized zirconia at 1600°C, however, results in nickel oxide diffusion into zirconia. The extent of nickel diffusion determines the degree of nickel loss in the final cermet structure and, possibly, has a negative effect on electrical (electronic) and mechanical (phase segregation) properties.

The new sintering furnace allows short sintering times at high temperatures, thereby reducing nickel diffusion and increasing mechanical properties of fuel electrode (tested by scraping with alumina edge), as well as increasing electrical conductance. For fuel electrode sintering, the stack support tubes are slipped over an alumina centering rod, that, in turn, is supported by alumina structures in the vertically mounted furnace. Fuel electrode resistance values of below $0.02 \Omega(\rho/\delta)$ at room temperature for 0.25 m long tube segments have been achieved. Such electrodes will exhibit $0.1 \Omega(\rho/\delta)$ at 1000°C.

Conclusions

The fabrication equipment to produce long fuel electrodes for 10 watt stacks is in place and five fuel electrodes of 0.25 m length each, have been sintered, which show good mechanical and electrical properties. These tubes will be used for interconnection EVD experiments.

5.1.3 Subtask C. Air Electrode Fabrication

Our present work is directed toward increasing indium oxide porosity without undue loss of conductivity. This goal has recently been achieved by the seeding technique. This technique involves the attachment of small indium oxide particles to the stack tube before it is inserted into the CVD reactor. Indium oxide will nucleate during the CVD reaction on these particles, leaving holes in areas that resist nucleation due to reactant starvation in such areas. The degree of porosity can be controlled by the number and size of these particles, as well as by temperature and exposure time to the CVD reaction.

The seeding is accomplished by spraying the stack tube with a thin layer of oil, or glue, to enhance the sticking of oxide particles that are dusted through a sieve onto the stack surface. The forces of adhesion are sufficient, even when oil or glue is burned off in the CVD reactor. During the first few seconds of oxide deposition, the nuclei are fixed by the new deposit and stack rotation in the reactor can be started without fear of seed shedding. This rotation and shifting of stack position results in uniform films and eliminates the negative effects of possible stratification of reactant vapors in the cross-flow CVD reactor.

Conclusion and Future Work

Stacks of the 10 watt size (0.3 m long) can be coated with porous indium oxide current collectors, that meet performance requirements with respect to porosity and conduction. Porosity optimization has yet to be performed in a series of seeding experiments.

5.1.4 Subtask D. Porous Support Tube Refinement

In-house fabrication of high-quality porous support tubes will be refined and analyzed with respect to pore distribution and gas diffusion characteristics in the finished product. Long tubes of 0.3 m in length will be fabricated for the 20 cell stacks.

5.1.4.1 Support Tube Fabrication

Process improvement in refining the fabrication of support tubes is continuing from powder preparation through each step of processing to the last step of firing. Support tubes, 0.15 m in length, will be fired in the standard pot furnace until the new furnace is available for fabrication of porous support tubes.

The porosity of the different groups of fabricated support tubes were in the 26-28 percent and 30-31 percent range. Specific

gravity of sintered tube material of the groups of different tube batches was in the 5.1 to 5.24 g/cc range. Thermal expansion of the calcia-stabilized zirconia material $(\text{ZrO}_2)_{.85}(\text{CaO})_{.15}$ was $10 \times 10^{-6} \text{ m/m/}^\circ\text{C}$.

5.1.4.2 Furnace Operation

Preparation and firing of longer tubes (0.3 - 0.6 m) have been delayed, due to relocation of the furnace into a newly-assigned laboratory area. Firing schedule of the new furnace is being evaluated and heating characteristics of the new furnace are being determined.

Figures 5.7, 5.8, and 5.9 show the arrangement for firing the support tubes in the new furnace. Extruded tubes are provided with a collar in order to hang them into a support plate, that is seen in top view in Figure 5.7.

Figures 5.10, 5.11, and 5.12 are views of the furnace in the newly assigned laboratory area, showing details of the furnace during a start up heating cycle. Trial runs are in process to determine the length of the heating cycle to fire nine support tubes, each ~0.6 meters long.

5.1.4.3 Summary

A new high-temperature furnace was constructed and made operational to fire support tubes ~0.6 meters in length. Additional time was spent in the design and relocation of the furnace support systems to a newly assigned laboratory area. Porous support tubes of three different wall thicknesses (0.065, 0.055, 0.045 inch) were successfully extruded from the new extrusion die sets. Fabrication of tools and fixtures necessary to extrude and process ~0.6 m long support tubes have been completed.

5.1.5 Subtask E. Cell Stack

Work in this area during the present quarter was related to preparation of interconnection layers of proper composition onto 20 cell stack configurations. Completed cell stacks will await further refinement of the EVD process, as described in Section 5.1.1.3.

Arrangement of support
Fig. 5.7 tubes, sample holder,
and muffle to be placed
into furnace cavity for
firing.

Fig. 5.8 Support tubes in the
process of loading in
furnace before firing.

Fig. 5.9 Overview of support
tubes in furnace
before firing.

Fig. 5.10 Location of high temperature gas kilns in newly assigned laboratory.

Fig. 5.11 Exhaust and manifold support system for new gas kiln.

Fig. 5.12 Start up of new high temperature gas kiln showing two propane/oxygen burners.

5.2 TASK 2. LIFE TESTING OF CELL COMPONENTS AND STACK

The purpose of this task is to evaluate the nature and extent of long-time stack deterioration due to mechanical and/or chemical component interaction. The goal of this task is life prediction of cell stacks, using state-of-the-art components.

5.2.1 Life Test Facility

Construction of the fuel cell life test facility has begun and the necessary laboratory modifications, involving plumbing, sheetmetal and electrical work should be completed by the end of October. Components needed for the implementation of the test system have been specified and ordered. A majority of the parts have already been received. Five furnace control panels, containing the power supplies, pyrometers, variacs, and controllers, are now being assembled. A data acquisition system, capable of monitoring 150 channels of information, has been ordered and delivery is expected within two months. The fully instrumented facility should be completed and ready to accept battery stacks for testing by the end of this year.

5.2.2 Subtask A. Interconnection Testing in a Dual Atmosphere

Work in this area is awaiting the preparation of suitable interconnections by the technique that will be used to fabricate 20 cell stacks.

5.2.3 Subtask C. Air Electrode-Interconnection Interaction

Indium oxide in the indium oxide/lanthanum chromite/nickel interconnection "sandwich" may be partially reduced (deoxidized) next to its interface with lanthanum chromite if the indium oxide layer is not sufficiently porous to permit rapid permeation of oxygen to that interface. This is a consequence of a small solid state oxygen permeation through the lanthanum chromite. Although the permeation of oxygen by solid state diffusion in pure lanthanum chromite is low, it is enhanced by the combined effect of doping with magnesium and contact with a reducing

(fuel) atmosphere at the fuel electrode sides of the interconnection. In the state of partial reduction, volatile In_2O and SnO species are lost from $\text{In}_{1-y}\text{Sn}_y\text{O}_{3-x}$ and this action may damage the electrical contact at the indium oxide/lanthanum chromite interface.

To alleviate this problem, we are developing methods to increase the physical porosity of the In_2O_3 layer and are studying the effect of oxygen partial pressure on both reversible oxygen loss and volatilization from pure and doped indium oxide. The latter studies are made by direct, in-situ measurements of weight changes of the indium oxide in a flowing gas atmosphere, using a controlled atmosphere, high temperature, microweighing system, previously described.⁽¹⁾

The initial results of these studies show significant volatilization from both In_2O_3 and $\text{In}_{1.96}\text{Sn}_{.04}\text{O}_3$ at oxygen partial pressures below about 10^{-7} atmospheres. In addition a reversible oxygen loss occurs which is much greater for the tin-doped than the undoped indium oxide. Figure 5.13 shows a comparison of the reversible oxygen losses which occur over the range 1 to 10^{-7} atmospheres oxygen partial pressure at 1000°C for these materials. The data suggest that pure In_2O_3 does not depart from the nearly ideal stoichiometry until the oxygen partial pressure is less than about 10^{-3} atmospheres. In contrast, $\text{In}_{1.96}\text{Sn}_{.04}\text{O}_3$ does not appear to be stoichiometric, even at 1 atmosphere of oxygen. This could be due to either a deficiency or an excess of oxygen since the C-type, rare-earth crystal structure of In_2O_3 contains unused but ordered sites of the proper size and location to accommodate extra oxygen ions. In this case the charge compensation is provided by Sn^{4+} ions which have a higher charge than In^{3+} which they replace. If excess oxygen can indeed be incorporated in the In_2O_3 lattice, a higher solid state permeation rate, due to diffusion of these oxygen ions, may be possible. This could improve the access of oxygen to the indium oxide/lanthanum oxide interface.

Fig. 5.13 - Loss of oxygen from indium oxides at 1000°C

5.3 TASK 3. STACK PERFORMANCE EVALUATION

This task is concerned with the testing of cell stacks under a variety of conditions to which they might be exposed in the operation of an envisioned power plant. The current-voltage characteristics of the stacks will be measured under three conditions: normal air and fuel conditions, rich and lean air and fuel conditions (including the water component of fuel) and interrupted current conditions. These measurements will aid in determining the magnitude and type of voltage losses associated with the individual stack components, and their contribution to the operational characteristics of the stack. Because of their diagnostic value, the tests will also be used for the cells in Task 1, (Subtask E), Task 2 (Subtask D) and Task 2 (Subtask E).

In order to interpret the measurements it would be very helpful to have an elementary theory for the current-voltage characteristic (V-I curve) which correctly predicts the qualitative features of our experimental stack data. An attempt to construct such a theory is given below, with results which are interesting and perhaps surprising.

5.3.3.1 V-I Characteristic Theory for a HTSOE Fuel Cell with H_2-H_2O Fuel

Ideally the terminal potential, V , of a fuel cell would have the form

$$V = E_0 - IR_0 \quad (1)$$

where E_0 is the theoretical (thermodynamic) open circuit potential of the cell, I is the current being drawn and R_0 is the ohmic internal resistance. In practice, the form is found to be rather

$$V = V_0 - IR_0 - \eta(I) \quad (2)$$

where the open circuit potential, V_0 , is somewhat less* than the theoretical value, E_0 , and an additional voltage loss term, $\eta(I)$, is included to describe the effects of various electrochemical polarizations occurring at the electrodes.

*Some reasons for this are discussed in Section 5.3.4.5.

A major assumption of our treatment is that the overpotential term, $\eta(I)$, arises only from simple concentration polarization losses in the electrodes when the fuel is hydrogen-water. Justification for this assumption will not be given here; a pertinent reference is the work of Etsell and Flengas.⁽³⁾ Other assumptions are made.

- Excess fuel and air are used so that depletion gradients in the supply system are negligible.*
- The ohmic resistance term, R_o , includes the electronic resistance of the air electrode, fuel electrode, and interconnection, plus the ionic resistance of the solid electrolyte.
- Lumped parameters are used in the equations.

The schematic in Figure 5.14 shows the pertinent component gas fluxes and partial pressures. At the air electrode the concentration overpotential, η_{air} , is given by the Nernst equation**

$$\eta_{air} = \left[\frac{RT}{4F} \right] \ln (P_{O_2} / P_{O_2}')$$
(3)

where R is the gas constant, T the absolute temperature, and F is the Faraday constant.

At the fuel electrode an analogous expression holds for the overpotential:

$$\eta_{fuel} = \left[\frac{RT}{4F} \right] \ln (P_{O_2}' / P_{O_2(fuel)})$$
(4)

*This assumption is easily satisfied in experimental tests; however it does not hold when one is dealing with a fuel cell stack having nearly complete hydrogen combustion, as would occur in a working power plant. A straightforward extension of the theory presented here enables one to deal with this case.

**In each of the overpotential equations presented here, the ratio of partial pressures will be chosen so that the overpotential is positive for normal cell operation.

Fig. 5.14- Schematic of the mass transport flows in an idealized high temperature solid electrolyte fuel cell, operating with hydrogen-water fuel. The unprimed variables are air or fuel component partial pressures as supplied to the cell; the primed variables are partial pressures at the solid electrolyte-porous electrode interfaces.

However, it is more useful to write the oxygen partial pressures here in terms of fuel component partial pressures. Since the reaction $\text{H}_2 + 1/2 \text{O}_2 \rightleftharpoons \text{H}_2\text{O}$ implies that

$$p_{\text{O}_2(\text{fuel})} = \frac{1}{K^2} \left[p_{\text{H}_2\text{O}}/p_{\text{H}_2} \right]^2 \quad (5)$$

where K is the equilibrium constant, the fuel electrode concentration overpotential can be written as

$$\eta_{\text{fuel}} = \left[\frac{RT}{2F} \right] \ln (p_{\text{H}_2}/p_{\text{H}_2}') + \left[\frac{RT}{2F} \right] \ln (p_{\text{H}_2\text{O}}'/p_{\text{H}_2\text{O}}) \quad (6)$$

The forms of this equation suggests labelling of the two terms as follows:

$$\eta_{\text{fuel}} \equiv \eta_{\text{hydrogen}} + \eta_{\text{water}} \quad (7)$$

and thus the total concentration overpotential, η , becomes

$$\eta = \eta_{\text{air}} + \eta_{\text{hydrogen}} + \eta_{\text{water}} \quad (8)$$

It will be shown that, typically, the air and hydrogen concentration overpotentials predominate at high currents, while the water concentration overpotential predominates at low and medium currents.

The final step in obtaining a working equation for the V-I characteristic requires that we link the partial pressures at the electrolyte interfaces (p_{O_2}' , p_{H_2}' , $p_{\text{H}_2\text{O}}'$ in Figure 5.14) with the cell current, I , being drawn. First, it can be shown that the gas fluxes through our electrodes are controlled by pore diffusion rather than viscous or molecular flow. This implies that for each component gas, an approximately linear relation

$$\text{flux} \propto \text{partial pressure difference} \quad (9)$$

will be valid. Second, each component gas flux is directly or indirectly linked to charge transfer at the electrodes, e.g., $1/2 \text{O}_2 + 2e \rightleftharpoons \text{O}^-$ and $\text{O}^- + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + 2e$; this implies for each component gas

$$\text{flux} \propto \text{cell current} \quad (10)$$

and hence

cell current $\propto$ partial pressure difference

Explicitly one has

$$I = S_{O_2} (P_{O_2} - P_{O_2}') = S_{H_2} (P_{H_2} - P_{H_2}') = S_{H_2O} (P_{H_2O}' - P_{H_2O}) \quad (11)$$

where the S's are proportionality constants having the dimensions, mA/, atm. They are essentially component gas diffusion conductances for the electrodes, expressed in terms of charge flow rather than mass or volume flow.*

Finally, by substituting (11) in (3), (4) and (6) one has

$$\eta_{air} = \left[\frac{RT}{4F} \right] \ln \left[\frac{S_{O_2} P_{O_2}}{S_{O_2} P_{O_2} - I} \right] \quad (12)$$

$$\eta_{hydrogen} = \left[\frac{RT}{2F} \right] \ln \left[\frac{S_{H_2} P_{H_2}}{S_{H_2} P_{H_2} - I} \right] \quad (13)$$

$$\eta_{water} = \left[\frac{RT}{2F} \right] \ln \left[\frac{S_{H_2O} P_{H_2O} + I}{S_{H_2O} P_{H_2O}} \right] \quad (14)$$

and from Equations (2) and (8),

$$V = V_o - IR_o - \eta_{air} - \eta_{hydrogen} - \eta_{water} \quad (15)$$

These last four equations summarize our theory of the V-I characteristic for hydrogen-water fuel.

*An exact treatment of the S's requires an analysis of component counter-diffusion (H_2-H_2O , O_2-N_2) within the electrode pores and will not be discussed here.

5.3.3.2 Qualitative Behavior of the V-I Characteristic

Interesting non-linear behavior in the V-I characteristic arises from the electrode overpotentials η_{air} , η_{hydrogen} , η_{water} , described by Equations (12), (13), and (14). Their important features are listed in the following:

5.3.3.2.1 Air and Hydrogen Overpotentials

- They produce curvature in the V-I characteristic which is concave downward.
- They have limiting currents which correspond to O_2 or H_2 starvation at the electrode-electrolyte interfaces.
- For typical fuel cell parameters they are nearly linear at low to moderate currents and become rapidly non-linear (and large) at high currents.

5.3.3.2.2 Water Overpotential

- o It produces a curvature in the V-I characteristic which is concave upward.
- No limiting current occurs; H_2O pressure at the electrode-electrolyte interface can become large.
- For typical fuel cell test parameters, this over-voltage is significantly large and non-linear at low currents; it increases relatively slowly at high currents.

An example of the V-I characteristic and the contributions of the various overpotentials are shown in Figure 5.15. These curves were calculated from Equations (12) through (15) for a hypothetical fuel cell with the parameters listed. Since the usual range for operation and/or life testing with this cell would be below a maximum current of approximately 1000-1200 mA, the relative importance of the water concentration polarization compared to that of air or hydrogen is evident.

Fig. 5.15 – Theoretical behavior of the current-voltage characteristic for a cell, showing the ohmic and concentration polarization voltage losses. For this example the air electrode concentration polarization is assumed negligible; when present it is very similar to the hydrogen concentration polarization in behavior.

5.3.3.3 Comparison of Theory with Early Stack Data

An important simplification in the equations can be made for the case where the cell current is well below (<one-half) the limiting air or hydrogen polarization currents. This is often the case for the usual stack tests. Equations (12) and (13) for the air and hydrogen overpotentials are then almost linear with current and can be written

$$\eta_{\text{air}} \approx \left[\frac{RT}{4FS_{O_2}P_{O_2}} \right] I \equiv R_{\text{air}}I \quad (16)$$

$$\eta_{\text{hydrogen}} \approx \left[\frac{RT}{2FS_{H_2}P_{H_2}} \right] I \equiv R_{\text{hydrogen}}I \quad (17)$$

i.e., as far as the DC current-voltage characteristic is concerned, the air and hydrogen polarizations behave like ohmic resistances R_{air} and R_{hydrogen} , defined above. This allows us to write the V-I characteristic equation for low-to-moderate currents as

$$V = V_0 - IR_1 - \left[\frac{RT}{2F} \right] \ln \left[\frac{S_{H_2O}P_{H_2O} + I}{S_{H_2O}P_{H_2O}} \right] \quad (18)$$

where

$$R_1 = R_0 + R_{\text{air}} + R_{\text{hydrogen}} \quad (19)$$

so that one now has only one non-linear term, the water overpotential.

Consider, now, the data for our first operating five-cell stack, presented in the previous Final Report of our initial contract.⁽⁴⁾ After 2 hours of operation the DC current-voltage characteristic for the stack was experimentally determined (approximately two dozen data points were taken). In addition, interrupted-current measurements were taken to determine the ohmic resistance of the stack, R_0 . A least squares fit of Equation (18) to the data was carried out with the results shown in Figure 5.16. It is seen that by the proper choice of parameters V_0 , R_1 ,

Fig. 5.16 — Comparison of experiment (points, dashed line) and theory (solid lines) for the current-voltage characteristic of a stack with hydrogen-water fuel. The lower theoretical curve includes the water polarization loss discussed in the text.

and S_{H_2O} , a good fit of the V-I characteristic was achieved. In addition, the value of R_l required, 1.55 ohms, was just slightly larger than the experimentally determined value of ohmic resistance, R_o , which was 1.46 ohms. This is consistent with relatively small air and hydrogen overpotentials (small values for R_{air} and $R_{hydrogen}$) which was postulated earlier.

It is interesting at this point to estimate from the theory what the voltage losses were in our experimental stack for a load current of 1000 mA:

Open circuit voltage	, 5.13 volts
Ohmic loss	, -1.46
Air + hydrogen polarization,	-0.09
Water polarization	, -0.75
Output voltage	, 2.83 volts

One should remember that the principal reason for the large water polarization is the small water content (3%) of the fuel. For fuels with higher water content, both the open circuit voltage and the water polarization will be significantly smaller. Nevertheless, an understanding of water polarization is essential for interpreting cell behavior and may be useful as a tool in cell testing.

5.3.3.4 Diagnostic Technique Suggested by the Theory

A standard diagnostic technique employed in fuel cell work is the current interruption method⁽⁵⁾ which enables one to determine the total overpotential, η , from both electrodes.* To determine the separate fuel and air electrode contributions, η_{fuel} and η_{air} , requires a suitable reference electrode. For a single thin film fuel cell this is difficult; for a multi-cell stack it becomes experimentally impractical.

One promising application of the theory is in a technique for determining the overpotential components η_{air} , $\eta_{hydrogen}$, and η_{water} for

*More precisely, it enables one to determine the total overpotential due to slow electrochemical processes, such as concentration polarization.

single or multi-cell units with no additional electrodes. According to Equations (12), (13), and (14), each overpotential component depends on a different fuel or air component partial pressure, provided the current is held constant. Therefore, measurement of the total overpotential at constant current for two (or more) values of a fuel or air component partial pressure should enable one to determine the corresponding overpotential and its pore conductance coefficient, S .

Suppose, for example, that one fixes the current at I and measures two values* of P_{O_2} ; then, according to equations (8) and (16)

$$\Delta\eta = \Delta\eta_{\text{air}} \approx \left[\frac{RTI}{4FS_{O_2}} \right] \Delta(1/P_{O_2}) \quad (20)$$

so that the air overpotential is

$$\eta_{\text{air}} \approx \frac{1}{P_{O_2}} \frac{\Delta\eta}{\Delta(1/P_{O_2})} \quad (21)$$

and the pore coefficient is

$$S_{O_2} \approx \left[\frac{RTI}{4F} \right] \frac{\Delta(1/P_{O_2})}{\Delta\eta} \quad (22)$$

The partial pressure may be changed by substituting an inert gas having a similar diffusion coefficient. For example, to determine η_{air} , one might employ 20% O_2 + 80% N_2 and 40% O_2 + 60% N_2 as the mixtures; for determining η_{hydrogen} one might use 97% H_2 + 3% H_2O and 48% H_2 + 49% He + 3% H_2O ; and for η_{water} one could use 10% H_2O + 90% H_2 and 5% H_2O + 5% N_2 + 90% H_2 . In each case only one active fuel or air component should be varied.

*Note that the changes in P_{O_2} may be large provided one does not approach low pressures where $P_{O_2} \sim I/S_{O_2}$; in that case, one would have to use the exact non-linear Equation (12) instead of the approximate linear Equation (16).

An interesting alternative to the use of interrupted current measurements for obtaining the change in total overpotential, $\Delta\eta$, is the following: From Equation (2) one has

$$\Delta\eta = \Delta V_o - \Delta V \quad (23)$$

Therefore if one measures both the change in open circuit potential, ΔV_o , and the change in cell potential, ΔV , under constant load, corresponding to a change in the partial pressure of a fuel or air component, then $\Delta\eta$ is obtained entirely by DC measurements.

Other diagnostic techniques based on the theory are possible and may be discussed in future reports. First, however, the theory should be tested by obtaining the complete V-I characteristic for a cell, measured for several different fuel and air compositions.

5.3.3.5 Effect of Inter-Cell Electrical Leakage on the Open Circuit Potential

In the Final Report⁽⁶⁾ it was pointed out that during the preparation of the fuel electrode, nickel oxide diffused into the stabilized zirconia of the porous support tube and increased its electronic conductivity. This would provide a current leakage path between adjacent cells and, consequently, reduce the open circuit potential below the theoretical value.

To determine whether these effects actually occurred, a section of porous support tube containing only fuel electrodes was tested. The specimen was placed in a hydrogen-water atmosphere and the leakage resistances (through the support tube) between two sets of adjacent fuel electrodes were measured over a temperature range of 400 to 1000°C. A wide range of applied potentials were employed (20 to 1000 mV) but the resistances measured were independent of the potential, and were nearly identical for the two sets of electrodes. A plot of this resistance as a function of temperature is presented in Figure 5.17. Activation energies for the conduction process were high, about 1.2 to 1.8 eV, and of the magnitude expected for electronic conduction in these oxides. At 1000°C the leakage resistance was about 45 ohms.

Fig. 5.17 — Leakage resistance between adjacent nickel fuel electrodes vs temperature. A hydrogen-water atmosphere was used

The effect of a leakage resistance of this magnitude on a cell comparable to those of the experimental five cell stack can be estimated. One would expect the open circuit potential, V_o , to be approximately 27 mV lower than the theoretical value, E_o . From the actual stack data one finds that V_o was about 38 mV lower than E_o . Considering the uncertainties in the electrode gap spacings and the diffusion of the nickel oxide which produced the leakage resistance, it is felt that this was reasonable agreement.

One concludes (1) that the fuel electrode preparation treatment introduces a moderate amount of electronic conductivity into the zirconia of the porous support tube, and (2) this provides a current leakage path between adjacent cells which results in a 3 to 4% reduction of the open circuit potential below the theoretical value.

6.0 FUTURE WORK

The following work plans are projected for the third quarter of the continuation contract, conforming to the projected task-time schedule of the present program.

6.1 TASK 1. DEVELOPMENT AND REFINEMENT OF FABRICATION PROCESSES

The goal of this task is to develop reliable techniques of component fabrication that will lead to reproducible stack performance.

6.1.1 Subtask A. Interconnection Fabrication by Electrochemical Vapor Deposition

Improvements made to the equipment and process toward proper adjustment of magnesium and aluminum concentrations in the deposited interconnection material, will be used to fabricate long tube cell stacks. Tubes with interconnection material deposited by RF sputtering will also be prepared and used for small (2-5) cell stack assemblies.

6.1.2 Subtask B. Fuel Electrode-Stack Process

The fuel electrode process has been refined to enable fabrication of up to 20 cell stacks to proceed.

6.1.3 Subtask C. Air Electrode Stack Process

Preparation of air electrodes by using seeding and non-seeding techniques will be tried. The aim here is to improve the air permeability through the air electrode current collector structure, toward attaining an optimum porosity/conductivity ratio in 20 cell stack lengths. However, this optimization is not considered of prime importance at this time. Its importance will be reassessed by performance analysis of 10 watt stacks.

6.1.4 Subtask D. Porous Support Tube

Process refinement of extruding porous, calcia-stabilized zirconia $[(\text{ZrO}_2)_{.85}(\text{CaO})_{.15}]$ tubes of 0.3 m length are continuing, with emphasis on techniques that will improve pore distribution and physical strength. A new furnace has been designed and constructed and is being used to fire tubes of ~0.6 meters in length, which will be used in preparing 20 cell fuel cell stacks.

6.1.5 Subtask E. Cell Stack

The aim of this subtask is to produce a reference 10 watt stack. Findings of Subtasks A through D will be used toward that objective.

6.2 TASK 2. LIFE TESTING OF CELL COMPONENTS AND STACK

The goal of this task is life prediction of cell stacks, using state-of-the-art components and material.

6.2.1 Subtask A. Interconnection Testing in a Dual Atmosphere

Dual atmosphere tests, designed to determine overpotential components in the fuel cell without the need of reference electrodes will be tried on fabricated fuel cells as they become available.

6.2.2 Subtask B. Fuel Electrode-Interconnection Interaction

The testing of fuel electrode-interconnection combinations to determine the nature of the interface resistance will continue.

An analysis will be made of the concentration polarization effects which may be expected from the porous substrate tube. Both the magnitude and time constant for the polarization will be estimated as a function of pore parameters.

6.2.3 Subtask C. Air Electrode-Interconnection Interaction

In the next quarter, further work will be conducted on volatilization losses. Also, alternate doping elements, which may improve the oxygen permeability of indium oxide, will be examined.

6.2.4 Subtask D. Single Cell Life Test

With successful fabrication of 20 cell fuel cell stack assemblies, life test evaluation of single cell (minimum) characteristics will be initiated on the life test apparatus, which should be operational by the end of the calendar year.

6.2.5 Subtask E. Small Stack Life Test

Stacks described in 6.2.4 Subtask D will be used here. Also, interconnections prepared by RF sputtering, will be evaluated here, if they can be successfully incorporated into finished cell stacks.

7.0 REFERENCES

7.0 References

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5. E. F. Sverdrup et al, "Hydrocarbon Fuel Cell Technology," p 311, Academic Press Inc., New York, 1965.
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APPENDIX A

PAST PROGRAM SUMMARY

Highlights of progress on the past contract program, conducted over two years (April 1, 1976 - March 31, 1978), are presented for the various tasks and subtasks, as specified in detail in the Design Plan of that program.⁽¹⁾

A.1 TASK 1. MATERIALS IDENTIFICATION AND SELECTION

A.1.1 Subtasks A and B. Interconnection Search and Identification

Work on the interconnection material identified a modified rare earth chromite as a very promising interconnection material. Specifically, modified lanthanum chromite, typified by the composition $\text{La}_{.95}\text{Mg}_{.05}\text{Al}_{.25}\text{Cr}_{.75}\text{O}_3$, was selected from among several systems studied, as having the most suitable properties for a cell interconnection material. No other oxide system investigated with comparable conductivity could be modified to produce the good thermal expansion match, low volatility, and negligible chemical interaction with other cell components that are available with this material.

As a result, this system received special effort in the second year of the program, to optimize its properties and to establish fabrication procedures for obtaining thin layer interconnection films. Films were successfully produced by electrochemical vapor deposition, initially onto fuel electrode substrates, and then as part of the fuel cell stack fabrication.

Additional work in this area was aimed at minimizing ionic transfer of oxygen ions through the interconnection layer, during cell operation.

A.1.2 Subtask C. Development of Other Stack Components

Selection of the other stack components was fixed during the first year of effort and work on them was primarily aimed at refining their fabrication into useful thin films. These materials are:

- support tube -- porous, calcia-stabilized zirconia (15 mol % calcia)
- fuel electrode -- nickel cermet (nickel deposited in a porous, stabilized zirconia skeleton)
- solid electrolyte -- yttria-stabilized zirconia (from 8 mole % to 12 mole % yttria)
- composite oxide air electrode -- tin-doped indium oxide (1 to 5 wt % SnO_2) current collector, with praeosodymium oxide impregnation of the zirconia skeleton.

A.2 TASK 2. FABRICATION TECHNIQUES

Techniques for producing films of the various active components proceeded to the level where they were used to produce fuel cells and fuel cell stacks. Concurrently, an extrusion process was developed to produce, in-house, the porous support tubes.

4.2.1 Subtask A. Interconnection

RF sputtering was used to produce films for basic property evaluations, whereas an electrochemical vapor deposition (EVD) technique was developed that produced modified rare earth chromite compositions that are both leak-tight and conducting, as thin films ($\sim 40 \mu\text{m}$). This EVD technique was subsequently used in fabricating the fuel cell stack that was tested on the program.

A.2.2 Subtask B. Electrolyte

The solid electrolyte, yttria-stabilized zirconia, was readily-prepared as a thin film by the EVD process. This process was reconfirmed on this program and was used to produce solid electrolyte films for the combination testing of components and fuel cell stacks.

A.2.3 Subtask C. Air and Fuel Electrode

Coating of zirconia support tubes with fuel electrode slurry compositions, along with subsequent nickel reduction in hydrogen, was reconfirmed as a viable process for producing the nickel-cermet, porous fuel electrode. This process was used in the preparation of the fuel cell stacks.

The CVD process was developed to a sufficient level to enable preparation of uniform films of tin-doped indium oxide air electrode current collector. This process was used in the preparation of the fuel cell stack that was tested in this program.

A.2.4 Subtask D. Porous Support Tube

Extrudable mixtures, prepared by combining selective size fractions of refractory starting powders and calcining at 1780°C, produced tubes that met the specifications of open porosity (>25 volume percent), tensile strength (>5000 psi) and thermal expansion ($\sim 10 \times 10^{-6}$ m/m°C at 1000°C). Surface pores of the tubes were $10^{1.1}$ μm in diameter with some variation in pore sizes, caused by agglomerates of water swelling starch plasticizers, used in the batch material preparation for extrusion.

A.3 TASK 3. COMPONENT TESTING

Equipment was built and used to test the fuel cell components and the fuel cell stack evaluated in this program.

4.3.1 Subtask A. Interconnection

Testing of interconnection films for composition and properties was ongoing throughout the program for gas tightness, resistivity, thermal expansion, doping level and oxygen vacancy concentration.

A.3.2 Subtask B. Combinations

A crossed electrode testing concept and specimen was evolved and equipment was assembled, to enable combinations of fuel cell components to be tested in various atmospheres.

A.3.3 Subtask C. Useful Life Testing

A 5 cell fuel cell stack was fabricated and evaluated on the program. Three series connected cells of this stack met the program goals -- displaying 80 percent voltage efficiency at 200 mA/cm^2 for 700 hours with less than 10 percent voltage degradation at 950° to 980°C in a hydrogen - 3 percent water vapor fuel atmosphere.

A.4 TASK 4. ALTERNATE ELECTROLYTES AND BATTERY DESIGNS

Work scheduled in this area involved:

- 1) keeping abreast of developments in the field, with regard to alternate electrolytes, and evaluating, in an initial manner, any that show promise to the Westinghouse thin film fuel cell.
- 2) modifying cell and cell stack design, if the test results indicated problems, particularly, with respect to mechanical over-stressing of cell or cell stack component(s).

No alternate useful electrolytes were developed in the solid electrolyte field during the 2 years of the completed program. Test data on the fuel cell stack was so favorable that no major design changes are being contemplated.

APPENDIX B

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

B.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 efficiency. Of all fuel-cell power systems, that based on a stabilized-zirconia, solid electrolyte offers the highest achievable efficiency. A battery design study, conducted prior to this program, indicated that power densities of 23 Kw/ft^2 of fuel cell module are achievable with the then state-of-the-art materials and fabrication processes when the stacks are operated at 80 percent electrical efficiency. The high-temperature solid-electrolyte fuel cell operates 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 operates at 1000°C for several reasons: a) the resistivity of the solid electrolyte is sufficiently low to permit high levels of electrical efficiency at high current densities and b) the heat released in the fuel oxidation can be efficiently transferred to the endothermic coal gasification reaction. Also, since coal is the basic fuel, if an economically competitive power plant, based on this fuel-cell type, can be developed, it will contribute to natural-resource conservation.

Apart from the efficiency advantage and the use of non-critical fuel, this fuel cell is attractive from other standpoints.

- Air pollution from the fuel cell power system is minimal. (Carbon dioxide and water vapor are the only species emitted.)

- The heat rejected by the fuel cell is employed to gasify coal, thus minimizing waste heat and avoiding thermal pollution of the environment.
- The fuel cell generating process does not require cooling water, consequently, siting of plants will 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 this program, the useful life of the thin-film battery had not achieved 100 hours. 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.

B.2 TECHNICAL BACKGROUND

Solid electrolyte fuel cells generate electrical energy from coal and air. In a coal-burning fuel-cell power system, means must be provided to:

- produce CO and H₂ fuel gases from the coal,
- clean and circulate these fuel gases to the fuel cells,
- transfer heat generated in the operation of the fuel cells to the endothermic coal gasification reaction.

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.

In this section a coal-burning fuel cell power system is described, including: (1) how solid-electrolyte cells produce electrical energy, (2) how individual cells can be combined to form high-performance batteries, and (3) how batteries can be combined with auxiliary equipment into a power 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.

B.2.1 How Solid Electrolyte Fuel Cells Generate Electricity

As shown in Figure B.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 inter-connection 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 . In contrast, the individual component layers lie in the thickness range of 20 to 50 μm .

Fig. B.1 - Schematic cross-section of a thin-film fuel cell

Exposed to the air flow is the air electrode. It is a composition of oxides, such as $(\text{In}_2\text{O}_3)_{0.98}(\text{SnO}_2)_{0.02}$ current collector, fabricated in a porous structure that is readily permeated by oxygen from air which flows over it. Praesodymium oxide is discontinuously deposited in a porous zirconia matrix that underlies the current collector and

represents the active part of the air electrode. This active PrO_2 effects the necessary $\text{O}_{2(g)}$ to 2O^- transition. Oxygen molecules from the air accept electrons at active PrO_2 sites, leaving the electrode positively charged, and forming oxygen ions, O^- , as shown in Fig. B.2. Each O_2 molecule removes four electrons and forms two O^- ions, as the cell operates.

Oxygen ions can enter the second component of the cell, a dense zirconia ceramic, such as yttria-stabilized zirconia. This is the solid electrolyte of the cell. At the operating temperature of 1000°C , oxygen ions pass through this layer, 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 will not conduct electrons, no 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, H_2 and CO , react with the emerging O^- ions to form reaction products, H_2O and CO_2 . 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 in 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. Electons will then flow from the ngative fuel electrode to the positive air electrode through the load circuit. Current can be drawn from a cell, as long as air and

- 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. B.2 - Schematic diagram of a solid electrolyte fuel cell, indicating how oxidation of the fuel generates electric current to the external load.

fuel gases are supplied and the combustion products removed. Current densities of nearly 300 mA/cm^2 can be obtained from solid-electrolyte cells, while still maintaining cell efficiency at 80 percent. The output voltage produced at such currents is a function of the ohmic losses and concentration polarization losses in the electrodes.

B.2.2 Fabrication of Fuel-Cell Stacks

To obtain the voltages required for a practical system, cells must be connected in series. The technique, illustrated in Fig. B.3, provides a potentially low-cost method of making a series-connected stack of cells. This modular stack design is aimed at minimizing ohmic losses at relatively high current densities. ^(8,7) It is necessary to provide an electrolyte surface area of approximately $5 \text{ ft}^2/\text{Kw}$, based upon state-of-the-art single cell performance.

Fig. B.3 - Cross-section of the Westinghouse thin-film solid electrolyte fuel-cell stack

A group of cells, each about 0.5 cm wide around a porous tube of about 1.3 cm O.D., are series-connected to form a stack. As schematically shown in the cross-section of Fig. B.3, all cells on the tube are series-connected by joining the air electrode of one cell to the fuel electrode of an adjoining cell, through an electronically conducting interconnection. The interconnection must be fabricated as a gas-tight film, just as in the case of the electrolyte. Particular attention must be paid to the junction between the electrolyte and interconnection films to ensure gas impermeability.

As indicated in the figure, a solid-electrolyte fuel cell stack consists of five components: an air electrode, a solid-electrolyte, a fuel electrode, and a cell interconnection, all approximately 50 μm , and a porous support tube with an approximate wall thickness of 1000 μm .

A design study at Westinghouse indicated that, in order to maximize the power generated per unit length of battery, the unit cell length must be approximately 0.5 cm. Fig. B.4 shows that the unit cell length is the sum of four characteristic lengths: ℓ_c , the active cell length; ℓ_i , the active interconnection length; and ℓ_a and ℓ_f , the gap lengths between adjacent air electrodes and fuel electrodes, respectively.

Fig. B.4 - Schematic of a unit cell design in the thin-film fuel cell.

The optimum active-cell and active-interconnection lengths, for the achievement of maximum power output, have been found to be dependent on the values of: (a) the resistivity-thickness products of the electrolyte and interconnection; (b) the resistivity-thickness ratios of air and fuel electrodes; and (c) the gap lengths, ℓ_a and ℓ_f . Precise fabrication processes, which will result in component films of the desired length and thickness in the appropriate location on the substrate, are, therefore, considered to be necessary for the fabrication of high-performance batteries.

B.2.3 High Temperature, Coal-Burning Fuel Cell System

A coal-burning, solid-electrolyte fuel cell system will include a coal gasifier, gas cleaning and circulating equipment, a fuel cell generator, a heat exchanger and a DC and AC inverter. Coal or coal char is fed to the coal gasifier, along with a portion of the hot CO_2 and H_2O combustion products and waste heat from the fuel cell generator (Fig. B.5). Here, coal reacts with the combustion products to form CO and H_2 fuel gases. The gases are fed to the fuel cell generator, after treatment to remove particulate material and sulfur compounds. In the generator, the fuel gases are electrochemically oxidized to CO_2 and H_2O .

The fuel cell generator operates at $\sim 1000^\circ\text{C}$ for the following reasons: (a) the resistivity of the solid electrolyte is sufficiently low ($\sim 20 \Omega \text{ cm}$) to permit high levels of electrical efficiency at high current densities, (b) the heat released in the fuel oxidation can be efficiently transferred to the endothermic coal gasification reaction.

A battery design study has indicated that power densities of 7 kW/ft^3 of fuel cell module are achievable with state-of-the-art materials and fabrication processes, when the stacks are operated at 80 percent electrical efficiency.

The air necessary for the operation of the generator is brought in separately. The N_2 of the air and the unreacted O_2 emerge from the

generator, exchange heat with the incoming air, and exhaust to the surroundings. Suitable AC power is available to tie into a utility grid network.

Fig. B.5 - Coal burning solid-electrolyte fuel cell power system.

APPENDIX C

TOLERANCE OF THE FUEL ELECTRODE TO SULFUR

Nickel or cobalt fuel electrodes in the high temperature solid state fuel cell will sulfidize at sufficiently high partial pressures of sulfur-containing gases. The concentration at which this damaging reaction will occur depends on some operating parameters of the fuel cell, in particular temperature, fuel composition, no-load voltage, and electrode polarization. The effect of the first three can be estimated from thermodynamic calculations. Earlier calculations of this type at Westinghouse are revised and extended here to include more recent data on the Ni/NiS_x phase boundary, to cover a broader range of fuel composition, and to examine the effect of operating at different temperatures. These parameters all have an important bearing on requirements for the engineering design of the fuel cell and the fuel pretreatment and purification system.

Nickel is being used as the fuel electrode in current work in preference to cobalt because it is a cheaper metal and can operate in leaner fuel mixtures without oxidation. However, cobalt will tolerate higher sulfur content of the fuel gases.

The basic results of the calculations are that a greater tolerance for sulfur-containing gas in the fuel is shown at (1) high temperatures, (2) higher hydrogen/water, as compared to carbon monoxide/carbon dioxide content of the fuel, and (3) at no load fuel cell voltages, either greater or less than a region near 0.7-0.75 volt. Figures C1, C2, C3, C4, C5, C6 illustrate this behavior.

Figure C1 shows the effect of the no-load fuel cell voltage on the sulfur concentration in the fuel at which the nickel electrode will just begin to sulfidize (i.e., the concentration of total sulfur-containing

Fig. C.1— Concentration of sulfur-containing gases at which a nickel fuel electrode begins to form $Ni S_x$ vs fuel cell voltage at 1000°C

Fig.C.2— Concentration of sulfur-containing gases at which the fuel electrode will begin to sulfide vs the fuel cell voltage

Fig. C.3— Tolerance of nickel electrodes to sulfidation as a function of fuel gas composition

Concentration of Sulfur-Containing Gases in Fuel at Which Nickel Fuel Cell Electrodes
Begin to Form NiS_x (PPM By Volume - Calculated)

Fig. C.4 - Tolerance of nickel electrodes to sulfidation as a function of temperature

Fig. C. 5— Concentration of sulfur-containing gases at which a nickel fuel electrode begins to form NiS_x vs fuel cell voltage at 700°C

Fig.C.6— Concentrations of sulfur-containing gases at Ni - Ni S_x phase boundary vs fuel cell voltage - calculated

gases in equilibrium with both nickel and nickel sulfide at the phase change boundary). These data are for 1000°C, which is near the highest operating temperature of the present fuel cell and for an arbitrary chosen fuel composition. A minimum in the curve, of about 90 ppm of sulfur-containing gases, is seen between about 0.70-0.75 volts. For normal operation of between about 0.6 and 1.0 volts then, this is the critical region where the least tolerance for sulfur content in the fuel gas occurs. If we allow for a 30% safety factor, these data suggest that 60 ppm or less would be a useful operating level for sulfur-gas content under these conditions. To increase this tolerance it would be necessary to operate at higher temperatures or higher hydrogen/water contents, as will be illustrated in the subsequent discussion.

Figure C2 compares cobalt to nickel for the same operating parameters. It is seen that cobalt has more than five times the sulfur tolerance of nickel at the minimum point of the curve, which would make it particularly useful, where high sulfur content of the fuel cannot be avoided, and at lower temperatures, where the sulfur tolerance of the fuel electrode is drastically reduced.

Figure C3 shows the effect of changing the volume per cent of H_2/H_2O in a hypothetical fuel gas containing only H_2O , H_2 , CO and CO_2 . It is seen that the tolerance minimum for fuel cell operation varies by about a factor of seven for the entire composition range, with the H_2/H_2O rich fuels having a greater sulfur tolerance than the corresponding CO/CO_2 -rich fuels.

Figure C4 illustrates the effect of temperature on the minimum tolerance of nickel for (total) sulfur-containing gases for the same fuel composition as previously illustrated for nickel at 1000°C (see Figure C1). A drastic reduction from a value of about 170 ppm at the Ni/NiS_x phase boundary at 1100°C to about 5 ppm at 700°C is seen. Thus, if any cell or stack of the fuel cell assembly were to operate at a temperature as low as 700°C, the fuel feed to the whole fuel cell system

would require a very low sulfur content. This suggests strongly that the operating temperature be kept high to reduce potential problems of electrode damage by sulfidation and the cost of removing sulfur from the fuel gas.

Figure C5 illustrates specifically the sulfur tolerance at 700°C for a system analogous to that previously illustrated (Figure C1) for nickel at 1000°C. (700°C is probably the minimum temperature at which we could usefully consider operating the present solid state zirconia-electrolyte fuel cell.) The minimum is seen not only to have shifted to a much lower ppm value, but also to have broadened and shifted to a somewhat higher voltage. For example, at 0.8 volt the value for the Ni/NiS_x boundary is about 8 ppm, only 3 ppm above the minimum. Thus, even raising our voltage operating range to 0.8-1.0 volt would not help much if we chose this relatively low operating temperature for any of the stacks or cells.

Finally, we show in Figure C6 the relative importance of the major gaseous sulfur-containing species in the fuel for the same conditions as illustrated for nickel (see Figure C1) at 1000°C. It is seen that CS_2 and S_2 are relatively unimportant over the entire voltage range of the fuel cell. H_2S followed by COS are the important species at the higher voltages (e.g., 0.8 volt and above) while SO_2 is the most important sulfur-containing gas species below 0.7 volt.

The data shown here illustrate the general magnitude of sulfur-containing gas concentrations which can cause sulfidation of the fuel electrode over varying operating parameters of the fuel cell stack. The general results are summarized* as follows:

- 1) Nickel or cobalt fuel electrodes should show a minimum tolerance for sulfur-containing gases at a fuel cell (no load) voltage between 0.7-0.75 volts depending on the temperature.
- 2) Fuel gases higher in $\text{H}_2/\text{H}_2\text{O}$ as compared to CO/CO_2 show a higher sulfur gas tolerance.

*These data consider only possible sulfidation effects and not chemisorption on the electrode surface.

- 3) Fuel electrodes (nickel or cobalt) show a much higher sulfur gas tolerance at 1000°C as compared with 700°C.
- 4) Cobalt electrodes show a considerably higher sulfur gas tolerance than nickel electrodes.
- 5) The major sulfur gas species in a fuel gas of the fuel cell are expected, thermodynamically, to be SO_2 at voltages below 0.7 volt and H_2S and, to a lesser extent, COS at voltages above 0.8 volt (no load voltage).
- 6) As a typical example, for a fuel gas composition $\text{H}_2 + \text{H}_2\text{O} = 25$ volume % and $\text{CO} + \text{CO}_2 = 75$ volume %, sulfidation of nickel will occur at about 90 ppm total sulfur-containing gas at atmospheric pressure and 1000°C and at about 5 ppm at 700°C at the minimum tolerance, which occurs in the no load fuel cell voltage range of about 0.7-0.8 volt.

10.0 Permanent Record Book Entries

Figuring Books, containing information described in this report are:

208043, pp. 103-127

208371, pp. 46-61

207773, pp. 76-83

204414, pp. 36-66

208337, pp. 66-182

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