Thin Film Battery/Fuel Cell Power Generating System

Seventh Quarter Report
Task E2
Project Status Report for the
Period October 1977 - December 1977

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MASTER

Prepared for the United States Department of Energy
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by

Research and Development Center
WESTINGHOUSE ELECTRIC CORPORATION
Pittsburgh, Pennsylvania 15235

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1.0 Abstract

The direct imaging, mass analyzer has detected the presence of a minor second phase in the candidate interconnection material, $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$. Since second phases can, conceivably, result in localized strain areas in the interconnection material (danger of crack formation), present work is aimed at its elimination, by revised doping procedures and/or substitution for the Mg^{2+} by Sr^{2+} , Ca^{2+} or Ba^{2+} . Other work on the candidate interconnection material suggests that low doping levels of the alkaline earth substituent should reduce the oxygen vacancy content, thereby reducing the diffusion rate of oxygen through the interconnection material.

Electrochemical vapor deposition experimentation continues toward producing thin interconnection films of suitable properties. EVD parameters under investigation include: temperature-growth rate relationship, doping, halide delivery systems, ratios of halides and masking of the fuel electrode substrate. It was recently discovered that the best interconnection films that were fabricated (strontium-doped lanthanum chromite) have been produced under conditions where air may have leaked, through a faulty hose connection, into the deposition reactor. Therefore, process parameters are being reinvestigated, to simulate the conditions that may have prevailed during the air leak. Here, less complex interconnection films of alkaline earth element-doped lanthanum chromite will be produced again and evaluated.

New masking transfer tape materials are being investigated at the higher EVD temperature (1300°C), presently used, to produce interconnection films. The selected tape material(s) will be used in the fabrication of the fuel cells. Further work on fuel cell fabrication and testing is awaiting refinement of the EVD process to produce interconnection films.

Nickel-cermet fuel electrodes are being fabricated onto porous calcia-stabilized zirconia support tubes. The tubes are now being fabricated in-house, by extrusion, to desired property specifications.

Air electrode current collector work is now aimed at producing porous films onto zirconia tubes. Here, "seeding" of the tube surface with fine powder of tin-doped indium oxide indicates that preferential film growth can occur, to produce the film porosity needed for proper oxygen delivery to the air electrode.

The crossed electrode measurement technique has demonstrated the capability of measuring resistances in combination film specimens to the milliohm range. Dimensional refinements of this test sample will improve its sensitivity, which is being used to measure effects of oxidizing and reducing atmospheres on combination film test samples.

2.0 INTRODUCTION

Of all fuel-cell power systems that, based on a stabilized-zirconia solid electrolyte, offers the highest achievable efficiency.⁽¹⁾ With coal as the basic fuel, conversion efficiencies of over 50% are possible, if the fuel cell is integrated with the endothermic coal gasification process in order to provide necessary heat.

The high-temperature solid-electrolyte fuel cell operates at 1000°C without catalysts, on a carbon monoxide-hydrogen gas mixture, provided by the gasification of coal. If this fuel cell type can be economically developed into a competitive electrical power generating plant, other fuels, presently used to generate electricity, can be conserved.

Apart from the efficiency advantage and the use of non-critical fuel, this fuel cell has other attractive features:

- 1) air pollution from the fuel cell power system is minimal (carbon dioxide and water vapor are the only species emitted),
- 2) the heat rejected by the fuel cell is employed to gasify coal, thus minimizing waste heat and avoiding thermal pollution of the environment,
- 3) the fuel cell generating process does not require cooling water, therefore, siting of plants will not be dependent on plentiful water supplies.

3.0 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:

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

In Report C-1197-2, July 9, 1976, a coal-burning fuel cell power system was described, including: (1) how solid-electrolyte cells produce electrical energy, (2) how individual cells can be combined to form cell stacks in order to achieve high voltages and (3) how stacks can be combined with auxiliary equipment into a power plant. Also described in that report was the status of Westinghouse fuel-cell technology at the onset of the present DOE program. In addition, the major technical problems that must be resolved, to allow demonstration of a long-lived, high-performance fuel-cell stack, have been reviewed.

The commercial feasibility of this new fuel cell power system greatly depends on the useful life of the generator. The useful life of thin-film stacks, with cells interconnected in series, developed on other programs, has not exceeded 100 hours. However, F. J. Rohr, of Brown, Boveri & Cie AG, at the "High-Temperature Solid Oxide Fuel Cells" Workshop at Brookhaven National Laboratories in May 1977, described that one of their unit cell tests has operated at 1000°C for 34,000 h (4 years), including about 10 shutdown and restart cycles. The ERDA-directed, NASA-managed, Energy Conversion Alternatives Study, (ECAS), conducted at the Westinghouse Research Laboratories in 1975,

indicated that, for fuel-cell power systems to be competitive from an electricity-cost standpoint, the useful life of the fuel cell modules must exceed 30,000 hours.⁽¹⁾

4.0 THE PRESENT PROGRAM

The purpose of this two-year, DOE-supported research program under Contract No. EY-76-C-03-1197, is the demonstration of the technical feasibility of a high-temperature, solid-electrolyte fuel cell, building on the presently-existing technological base. The bulk of the work consists of identifying and selecting candidate component materials, fabricating cells and cell stacks from these materials, and testing these cells and cell stacks under conditions which might be expected in operation. The major emphasis is on the invention and fabrication of an interconnection film, which has the following properties at 1000°C, the proposed temperature of stack operation:

- 1) chemical stability in air and fuel gas,
- 2) electronic resistivity in the working environment of less than 50 ohm-cm,
- 3) thermal expansion characteristics compatible with other components,
- 4) non-reactivity with adjoining components.

Emphasis is also being placed on the fabrication of porous support tubes of calcia-stabilized zirconia, to the desired specifications of tensile strength, porosity, surface finish, and purity. Concurrently, tubes will be prepared in-house and, if necessary, will also be purchased from commercial suppliers and evaluated for compliance with the following specifications:

- 1) tensile strength of 5,000-10,000 psi,
- 2) open porosity of 25-30 volume percent,
- 3) no surface pore greater than 10 μ m in diameter.

The culmination of this program will be the fabrication and testing of a stack, consisting of a minimum of three interconnected cells. It is anticipated that the test data obtained from operating this stack, under simulated conditions, will permit an evaluation to be made of the technical feasibility of solid-electrolyte, high-temperature fuel cells, based on the materials and fabrication advancements derived from the program.

5.0 OVERALL TECHNICAL EFFORT

The overall technical effort is aimed at achieving 5 milestones in the 2 year period of the contract. These include: 1) identifying and selecting new candidate interconnection materials; 2) preparing porous support tubes to desired specifications; 3) demonstrating acceptable test performance in identified interconnection material(s) and acceptable test performance of all components; 4) in unit cells and 5) in cell stacks.

5.1 TASK 1. MATERIALS IDENTIFICATION AND SELECTION

The overall purpose of this task is to advance the state of the materials technology of the five components of the high-temperature (1000°C) solid electrolyte fuel cell. These components are the support tube, fuel electrode, electrolyte, air electrode and cell interconnection.

5.1.1 Subtask 1A. Interconnection Literature Search

This subtask identified five candidate systems of compounds:

- 1) alkaline earth chromite system
- 2) rare-earth chromite system
- 3) cerium oxide plus niobium (tantalum) oxides
- 4) alkaline earth titanate system
- 5) rare-earth nickel-cobalt-iron oxide systems.

Subsequently, the rare-earth chromite system, in particular lanthanum chromite, was selected for more intensive investigation to produce a satisfactory interconnection material.

5.1.2 Subtask 1B. Selection of Interconnection Materials

Modified lanthanum chromites, particularly $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$, have been selected as the candidate interconnection materials.

5.1.2.1 Chemical Characterization of Lanthanum Chromites

Substitution of alkaline earth ions for part of the La^{3+} or Cr^{3+} in lanthanum chromite is done to increase the conductivity. An appreciable substitution of Sr^{2+} , Ba^{2+} , or Ca^{2+} can be made in the A position of the ABO_3 perovskite structure, where the large La^{3+} ion normally resides. Similarly, the Mg^{2+} ion substitutes readily in the smaller B position for Cr^{3+} . However, it is not known if small amounts of Mg^{2+} can substitute for the La^{3+} due to the large mismatch in ionic radii. Materials mixed to give the empirical formulations $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ and $\text{La}_{0.95}\text{Mg}_{0.05}\text{CrO}_3$ have been studied for MHD applications by others, and by us as possible interconnection materials for the fuel cell application. Increased conductivity of magnesia-substituted, as compared to unsubstituted, lanthanum chromite has been interpreted as indicating that at least some magnesia goes into solid solution. However, Anderson has suggested, on the basis of experiments of phase transition temperature changes in lanthanum chromite materials with different La/Cr ratios, that Mg^{2+} probably substitutes at Cr^{3+} rather than La^{3+} sites in the crystal structure. In addition, small amounts of a second phase, containing Mg^{2+} , have been reported in a few instances by others in lanthanum chromite materials prepared for MHD studies.

To investigate this problem further, we are using samples of $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ prepared in two ways: (1) by repeatedly grinding, pressing, and sintering at 1700°C , pellets prepared by mixing the pure oxide component powders; (2) by a chemical preparation, resulting in an initially homogeneous product, as prepared for us by H. Anderson. Particular care was exercised in both preparations to produce materials with an empirical chemical composition very close to the stoichiometric formulation.

We previously reported⁽¹⁾ results of an X-ray diffraction study obtained by using monochromatic X-rays which failed to detect a trace of either MgCr_2O_4 or MgO in these materials. The technique was

sufficiently sensitive to detect less than one-half of the added magnesium if it were present as well-crystallized MgCr_2O_4 . However, the sensitivity to MgO detection, another possible second phase, was poor and its presence or absence could not be confirmed.

A more sensitive method for detecting the presence of magnesium in a minor second phase involves use of the Direct Imaging Mass Analyzer (DIMA). This examination, (see Fig. 1) lead to a number of observations.

- 1) Sample 1, prepared from the oxides, shows the presence of a separate magnesium and silica containing phase, the silica being an impurity. Fig. 1A shows the images which represent approximately 250 microns of surface of the oxide pellet. The Mg and Si show up as distinctly different spotty patterns, characteristic of a second phase. The La, Cr, and Al show similar patterns, representing the main lanthanum chromite phase.
- 2) Sample 2, the chemically homogeneous preparation which was hot pressed, shows in Fig. 1B no evidence of a second magnesium-containing phase, the patterns for Mg, Cr, and La being similar.
- 3) Sample 3, the chemically homogeneous preparation which was cold pressed and annealed at 1700°C for 2 hours shows in Fig. 1C a pattern for Mg which is similar to those for La and Cr but with a few extra spots. This suggests that a small amount of a second phase is beginning to form.

These data indicate that the preparation technique for magnesium-containing lanthanum chromite is important and that the magnesium might be present in a metastable solid solution state in some instances. This will require further study, regarding the nature, extent, and stability of solid solutions of the magnesium-containing lanthanum chromites.

Since the presence of a second phase, or its formation in the interconnection of the fuel cell during operation, could conceivably result in localized strain areas within the interconnection, it would be

A. Sintered $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$

B. Homogeneously formed $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$ hot pressed

C. Homogeneously formed $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$
sintered 2 hours at 1700°C

Fig. 1. Distribution of Mg, La, Cr, Al, and Si in $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$.
Data from the Direct Imaging Mass Spectrometer.

desirable to eliminate its formation. Our subsequent work will study the possibilities for eliminating the second phase by revised doping procedures which may include reducing the magnesium doping level, or by substitution of magnesium in both the La^{3+} and Cr^{3+} positions or by substitution of low levels of Sr^{2+} , Ca^{2+} , or Ba^{2+} for the magnesium.

5.1.2.2 Variation in Oxygen Content of Lanthanum Chromite

The interconnection layer in a thin layer fuel cell stack is subjected to extremes in oxygen partial pressure, ranging from 0.21 atmospheres oxygen partial pressure at the air electrode to as low as 10^{-18} atmosphere of oxygen at the fuel electrode. Under the fuel-rich condition, lanthanum chromite may lose oxygen from the crystal lattice. We previously reported high temperature microweighing experiments which showed an oxygen loss from $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_{3-x}$ of about $x = 0.01$ for an oxygen pressure of about 10^{-16} atm at 1000°C .⁽¹⁾ These conditions correspond to those present in a typical fuel mixture at the anode of a fuel cell with an open circuit potential of a little less than 1 volt.

In this report we have augmented those measurements to include a range of oxygen pressures between 0.21 atm (air) and 10^{-18} atm. Additional materials studied included a hot pressed sample of $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ and $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3$.

Weight changes as a function of oxygen partial pressure and temperature were made in an enclosed high temperature microweighing system previously described.⁽¹⁾ Hydrogen/water/nitrogen and oxygen/nitrogen mixtures were used to obtain the different oxygen partial pressures. Figs. 2 and 3 show results for the two lanthanum chromite compositions. It is seen that:

- 1) the oxygen content of both materials is relatively insensitive to further increase of oxygen pressure above about 10^{-8} atmosphere and temperatures of 1000°C , or below;
- 2) solubility of oxygen at low oxygen partial pressures decreases as the temperature rises;

Fig. 2—Oxygen deficit x in $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_{3-x}$ vs oxygen pressure assuming bulk absorption 1000 °C

Curve 693338-A

Fig. 3—Oxygen deficit x of $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_{3-x}$ vs oxygen partial pressure

- 3) oxygen vacancy concentration at 1000°C and low oxygen pressures is less for $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_{3-x}$ than for $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_{3-x}$ *
- 4) the maximum vacancy concentration does not exceed that which would result from complete charge compensation for the added alkaline earth constituent (i.e., $x = 0.025$ and $x = 0.08$, respectively, for the two compounds above);
- 5) the oxygen vacancy concentration in $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_{3-x}$ appears to be approaching a value closer to $x = 0.0125$ - 0.013 than the maximum of $x = 0.025$, which would be expected if all the magnesium were in solid solution. This is consistent with the observation from the Direct Imaging Mass Spectrometer which indicates that much of the magnesium may reside in a second phase, rather than in the lanthanum chromite, for this sample.

In contrast to the data shown in Fig. 2 for $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_{3-x}$, a sample, hot pressed from a material of the same composition which was prepared by a homogeneous chemical reaction, showed little weight change when subjected alternately to oxygen pressures of 0.21 and 10^{-18} atmospheres. Perhaps a surface barrier to oxygen diffusion forms on the hot-pressed sample. This sample shows a homogeneous distribution of magnesium in the oxide, while the sample used for the data in Fig. 2 shows presence of a considerable magnesium-containing second phase component in the Direct Imaging Mass Spectrometer. Other possibilities are a near-surface reaction for the sample of Fig. 2. Further experiments will be made to explain this contrasting behavior.

It seems reasonable to assume that Fig. 2 data do represent true bulk absorption from consideration of other data. For example, resistivity changes appreciably with change in oxygen partial pressures, suggesting a stoichiometry change. X-ray and neutron diffraction data

*This is to be expected based on the lower content of the alkaline earth substitution in the former compound.

of Khattak and Cox⁽²⁾ show that the crystallographic cell volume of strontium-doped lanthanum chromite increases when oxygen is removed by treatment in hydrogen at high temperatures. This indicates that a bulk absorption occurs in their material and should also be expected in our strontium-doped and, probably, in our magnesium-substituted lanthanum chromites as well.

Assuming that the data represent true bulk absorption, we may formulate an equilibrium relating the oxygen pressure and the activities (a) of the reacting ionic, electronic, and vacancy species in the oxide.

Consider the substitution of Sr^{2+} or Mg^{2+} into lanthanum chromite for either the La^{3+} or Cr^{3+} ions. The lower valence of the alkaline earth species requires charge compensation which would seem most likely to occur either by (1) formation of positive holes (h^+) (either free or associated with a Cr^{3+} ion) or (2) elimination of one O^{2-} and formation of a vacancy at an oxygen site ($\square_o$) for each two Mg^{2+} or Sr^{2+} added. This would result in an equilibrium of the form

if the hole is associated with a chromium ion, or the relation

if the holes are essentially uncomplexed. For (2) we write the equilibrium constant

$$K = \frac{(a\text{O}^=)^2 (ah^+)^4}{(P_{\text{O}_2}) (a \square_o)^2} \quad (3)$$

Considering $\text{O}^=$ is approximately constant for low concentrations of Sr^{2+} or Mg^{2+} and letting y = the molar concentration of Sr^{2+} or Mg^{2+} in the lanthanum chromite formula (e.g., $y = 0.16$ in $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_{3-x}$) and x = the concentration of oxygen vacancies, we may write

$$K P_{\text{O}_2} \approx \frac{(ah^+)^4}{(a \square_o)^2} \approx \frac{(y-2x)^4}{x^2} \quad (4)$$

This relationship approximately holds for $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_{3-x}$ if we assume that about 2.5 mole % of either the chromium or lanthanum in the lanthanum chromite is replaced by Mg^{2+} and adjust K for the best fit to the curve. The value $x = 0.025$ is only half that assumed by the empirical formulation $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_{3-x}$. However, since the Direct Imaging Mass Spectrometer data show that at least part of the magnesium is present as a second phase in the sample, this is not an unreasonable assumption. For $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_{3-x}$ for which concentration of positive holes is much larger, the experimental data deviate drastically from (4). The agreement becomes better at high vacancy concentration where the concentration of holes in turn becomes smaller. The data suggest that low doping levels of the alkaline earth substituent are desirable from the standpoint of reducing the oxygen vacancy content, which should also reduce the diffusion rate of oxygen through the interconnection.

5.1.2.3 Radio Frequency Sputtering of Interconnection Material

Depositions of the interconnection film formed by R. F. sputtering consisted of samples of zirconia with a nickel cermet fuel electrode and control samples of alumina with the interconnection layer $\text{La}_{0.75}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$. In general, these depositions were made at moderate substrate temperatures (400-450°C) at reduced power levels (200 watts), since irregularities are produced in films at higher temperatures and higher power levels (increased deposition rates).

It was found that the sputtered films of the interconnection material, when deposited at high substrate temperatures, were highly non-uniform. Large areas appeared "splotchy", indicating a lack of integrity in the film. In these areas, the adhesion to the substrate was good but the deposited film flaked off, with the separation occurring in the film and not at the film-to-substrate interface. This is probably due to some type of contamination during the run. Severe outgassing could be occurring from the tooling due to the high temperatures, or from portions of the powder target itself, due to a combination of high power and radiant heat from the hot substrate. Since only total system

pressure is monitored and this consists of added argon, ever large fluctuations in the partial pressure of various gases would not be detected. These could be sufficient to destroy the bonding within the deposited layer.

This problem is only severe at high substrate temperatures (600°C) and high deposition rates. It does occur at lower temperatures but is considerably reduced, since substrate temperatures of 450°C appear adequate to produce dense layers. In addition, a lowered deposition rate at this lower temperature also helps to produce a smoother film. The standard conditions for deposition are now 200 watts R.F. power input with a substrate temperature of 400-450°C. These conditions do not produce a good film on every run, but the yield (50 to 75%) appears adequate for the present work.

The powder target remains a problem and can be associated with the defect areas in the deposited film. The surface of the target often appears non-uniform after a deposition. This could be from vibrations associated with the mechanical pump and/or irregularities in the discharge itself. There has been a direct correlation between irregularities in the target and some of the deposited film layers. The standard procedure is to smooth out the surface of the target prior to each run and add fresh powder if needed, but this does not appear sufficient to eliminate the problem. A hot pressed target of this material was fabricated and should cure problems associated with the powder target. However additional problems (such as cracking due to uneven heating) might occur to the hot pressed target. Thus, for the immediate future, the powdered target will be used, accepting the present yield figure. In future work, the hot pressed target will be evaluated to determine its effect on deposited film quality.

5.1.3 Subtask 1C. Development of Other Stack Components

Other stack components include the fuel electrode, the air electrode and the solid oxide electrolyte.

5.1.3.1 Fuel Electrode Development

Nickel-zirconia cermet electrodes are the sole type of fuel electrodes presently considered in our studies. These electrodes will be used in all component tests, where applicable, and in cell and cell-stack tests. They consist of metallic nickel dispersed as a continuous phase in a porous yttria-stabilized zirconia skeleton, so as to render a solid structure of 40 volume % nickel and 60 volume % zirconia. The fuel electrode layer contains nearly 30% void volume, and an average pore size of 3 to 4 μm for fuel gas encroachment.

5.1.3.2 Air Electrode Development

Development work has placed emphasis on the fabrication of tin-doped indium oxide current collectors for the air electrode, primarily because this material has a thermal coefficient of expansion ($9.23 \times 10^{-6} \text{ m/m/}^\circ\text{C}$ at 1000°C), favorably matching that of the zirconia support tube ($\sim 10 \times 10^{-6} \text{ m/m/}^\circ\text{C}$ at 1000°C).

5.1.3.3 Solid Oxide Electrolyte Development

Yttria-stabilized zirconia ($\sim 10 \text{ w/o yttria } \pm 2\%$) is the preferred solid electrolyte composition that is being used in the preparation of multi-component thin film tests and will be used in unit fuel cells and fuel cell stack tests. Presently, no other electrolytes appear as promising and, therefore, no further solid electrolyte compositional development work is underway.

5.2 TASK 2. FABRICATION TECHNIQUES

The purpose of this task is to develop reliable techniques for the fabrication of gas-impermeable films of the candidate interconnection material(s), between the porous air and fuel electrode films, on the stabilized zirconia porous support tube structure. Also, the purpose is to optimize the fabrication of the electrodes and substrate components.

5.2.1 Subtask 2A. Interconnection Fabrication

Fabrication techniques that have been considered during the program for the interconnection materials include radio frequency (RF)

sputtering and electrochemical vapor deposition (EVD). Presently, work is centered on the EVD technique for fabricating modified lanthanum chromite interconnection films onto the nickel cermet fuel electrode.

5.2.1.1 Fabrication of Interconnection Films by Vapor Deposition of Modified Lanthanum Chromite

Initial vapor deposition experiments indicated that films of up to 50 μm thickness can be deposited by EVD at 1350°C. The films were identified by several techniques as LaCrO_3 . Although strontium was added to the vapor species in the form of SrCl_2 , it was not incorporated into the deposit to a noticeable degree. This fact was established by electrical measurements and Direct Imaging Mass Spectrography (see Sixth Quarter Report).

Subsequently it was attempted to grow magnesium and aluminum doped LaCrO_3 , with little success, with respect to achieving sufficiently thick films and achieving conductivity. In addition, experimental difficulties arose in the parallel and controlled delivery of four halides. Masking of substrates at 1350°C with oxide powder layers that were used successfully at temperatures up to 1200°C became an additional problem because the layers developed cracks, due to sintering of the oxide powders. These difficulties led to an intensified effort in the vapor deposition of modified lanthanum chromite that is not yet completed.

Fifteen deposition runs have been made during the seventh quarter at temperatures of 1300°C and higher. These runs explored the parameters:

- 1) temperature-growth rate relationship
- 2) doping (magnesium, aluminum, strontium)
- 3) halide delivery systems and ratios of halides
- 4) masking

Results of Vapor Deposition Experiments

During initial runs, an "erratic" leak developed in a hose connection which, depending on hose position, allowed air to infiltrate into the deposition reactor. It was under such conditions, that the

first 50 μm thick LaCrO_3 -film was deposited (without knowledge of the leak). The interpretation of the initial runs, therefore, is problematic. Following experiments were conducted with a thoroughly leak checked apparatus, and resulted in very thin coatings of less than 3 μm thickness. Further experiments were conducted under conditions that were considered to be possible during the initial leak situation. These included high carbon dioxide or carbon monoxide content in the reactor (air leak and reaction with graphite reactor lining) and valence change of chromium in the form of chromium II- or chromium III-chloride. Flow and pressure changes inside the substrate tube and in the surrounding reaction chambers were also investigated with the general result that only very thin, yet dense films were obtained.

At the time of this writing, the experimental investigation of leak-situation conditions, that produced a thick film, is not concluded. In order to avoid complicating an already complex situation, our experiments are being restricted to alkaline earth element(s) doped lanthanum chromite (aluminum doping will follow later).

Parallelling our deposition experiments, we did several masking experiments. We applied oxide powder layers to substrates by the tape transfer technique (Vitta Corp. tapes) and investigated tapes having chromium oxide, zirconium oxide (stabilized and unstabilized), magnesium oxide, and calcium zirconate. The best results were achieved with a 3 mil ($\sim 75 \mu\text{m}$) thick calcium zirconate tape, consisting of spherical particles of ~ 5 to $10 \mu\text{m}$). The powder layer, applied with this tape, will not sinter to the degree finer powder layers do, and test samples of sufficient quality are obtained for the present program. Further refinement is still required to achieve flawless masking.

Status of Vapor Deposition Experiments

Therefore it is obvious from the preceding discussion that the experimental state of the program is in a critical phase that is linked to the deposition of a usable, thick and conductive lanthanum chromite film. The fact that a thick film has been produced indicates

that it can be done, however the reproducibility of this result is of present, prime concern. Since a thick film was achieved during possible inflow of air (leaking into the reactor), it is not safe to assume at this time that the film grew by an EVD type mechanism. The possibility of a CVD type deposition, or a combination of both growth mechanisms (CVD and EVD), must be considered. These possibilities are presently under intense investigation.

Since the experimental evidence for the growth of lanthanum chromite by vapor deposition is not yet complete, a more detailed discussion and conclusions will follow in the next report.

5.2.2 Subtask 2B. Fabrication of the Solid Oxide Electrolyte

The solid oxide electrolyte film component of the fuel cell is fabricated by the electrochemical vapor deposition technique. This technique, described in detail elsewhere⁽³⁾, produces dense, leak-tight films of up to 40 μm thickness of yttria-stabilized zirconia, the candidate electrolyte material.

5.2.3 Subtask 2C. Air Electrode Fabrication

The development of the air electrode collector has continued with the chemical vapor deposition (CVD) of tin-doped indium oxide films and their characterization.

During this quarter, the efforts in the air electrode current collector development were directed at additional evaluation of the chemically vapor deposited (CVD) films of tin-doped indium sesquioxide. Also, exploratory CVD-experiments were tried on surface substrate modifications aimed at promoting preferential film growth to produce desired film porosity in the air electrode current collector.

Electrical resistivity, ρ , measurements of films deposited on stabilized zirconia substrates were obtained as a function of temperature. These data were an extension of those previously reported.⁽⁴⁾ It was discovered that the previous ρ vs T data represented the initial state of the as prepared film. When the films were annealed in air at 1000°C for more than 120 hours, a reversible behavior in the heating and cooling

ρ vs T curves was reached. Typical results of such a behavior are graphically shown in Figs. 4 and 5. These two films were annealed at 1000°C after the first thermal cycle of the ρ vs T measurements. Most of the annealing was done after the third heating. The data clearly show that most of the small changes in ρ at 1000°C occur during the first few hours. The reversible behavior, however, is achieved only after the aforementioned long annealing treatment (i.e., ≥ 120 hours). The type of temperature dependency of the resistivity below 750°C shown in the final reversible heating and cooling curves of these figures is typical of that of semimetallic conductors.

The present CVD exploratory type of experiments were aimed at testing the possibility of preferential film growth by the CVD-procedure on zirconia substrates that had been covered with grains of tin-doped indium sesquioxide. This seed-type oxide material was obtained from the preparations used for the vapor source samples. The first such CVD-experiment was carried out on a zirconia tube; only one area of this tube had been sprayed with the seed powder. The spraying was done after the surface was wetted with *n*-butyl acetate. The results of this experiment can be assessed by the photographs of the coated tube, typical micrographs in the two areas (powdered and non-powdered) and the resistance profile data of Fig. 6. The two micrographs from the portion of the tube that had the seed powder show areas of preferential film growth. The top micrograph represents the most desired case of porous film growth. The micrograph on the right side shows a typical area of the impervious film that grows on the right side of the substrate tube that did not have the seed. The effect of the seed powder on the type of film is also shown on the resistance profile of the coated tube that is shown in Fig. 6. This increase of resistance of films grown on surfaces seeded with grains of the same material had also been observed in previous CVD-experiments in accidental gas stream entrainment of powder of the tin-doped indium sesquioxide from the chamber of

Fig. 4— Resistivity versus temperature behavior of tin-doped indium oxide film deposited on bentonite doped calcia stabilized zirconia tube

Curve 692925-B

Fig. 5— Resistivity versus temperature behavior of tin-doped indium oxide film deposited on calcia stabilized zirconia tube [film thickness: 27.8 μm]

Fig. 6. Resistance Profile of Tin-doped Indium Oxide Film across Seeded and Non-seeded Sections of Calcia-stabilized Zirconia Tube (Run # IN_{II}-11).

the reactor. Such entrainment occasionally occurred in the early series of experiments when the vapor source oxide sample was used in the granulated form.

This idea of attempting to provide initial film nucleation sites was tried again on two other zirconia tubes. These tubes were sprayed with oil that contained the seed grains in suspension before their exposure to the gaseous stream of the reactants of the vapor deposition reaction. In each case and at film thicknesses of $\geq 20 \mu\text{m}$, porosity was absent. This was determined by microscopic examinations and pressurized tube leak tests. In one case, the final CVD film was obtained in two stages; during the first stage, $17.4 \mu\text{m}$ film thickness was obtained. Visual observations of this thin film indicated porosity. Due to this low thickness of this film, additional vapor deposition was carried out on this tube and a final thickness of $33.9 \mu\text{m}$ was reached. At this thickness, the film was impervious.

One difficulty that has thus far been observed is that of lack of good adherence of the seed powder on the substrate surface before its exposure to the reactant gaseous mixture of the vapor deposition process. The conditions of providing such grain seed adherence on the substrate have to be further established.

In some of our recent CVD-experiments unknown variables in the CVD reactor resulted in isolated, band type porous film areas on the zirconia substrate. Fig. 7 shows a micrograph of such an area. This micrograph clearly shows the desired porosity. Moreover, the measured resistance in these areas was higher than that of the impervious film zones on the same substrate. Investigation into the CVD-process variable(s) that caused such porous film strip areas to develop may provide the necessary modification in the CVD procedure to obtain the overall needed porosity for this application.

Conclusions

Prolonged annealing (≥ 120 hours) in air at 1000°C of the chemically vapor deposited tin-doped indium sesquioxide films on zirconia

Fig. 7 Porosity of Tin-doped Indium Sesquioxide Film Caused by Unknown Variable(s) During Chemical Vapor Deposition.

substrates is necessary to achieve reversible behavior in their electrical resistance upon heating and cooling. The attainment of film porosity by controlling the film growth process on the substrate surface through its initial coverage with seed grains seems feasible, although not conclusive, at this stage.

5.2.4 Subtask 2C. Fuel Electrode Fabrication

The fabrication sequences in preparing nickel cermet fuel electrode layers on the support tubes have been detailed.⁽⁵⁾

5.2.4.1 FABRICATION OF FUEL ELECTRODES ON IN-HOUSE TUBES

The availability of porous tubes, developed in-house under this program allowed the fabrication of fuel electrodes on these tubes. The first set of twelve tubes was coated with nickel-zirconia cermet layers under identical conditions used for tubes that were supplied by Zircoa Corp. The strength of the cermet layers on our tubes is reduced (tested by scraping the electrode film). It is assumed that this is a result of the impurities that are introduced into "Zircoa" tubes in the form of bentonite, which will form a liquid phase at the temperature at which fuel electrodes are sintered. This liquid phase sintering may aid in strengthening the fuel electrodes. Our tubes are of high purity and, therefore, result in electrodes of less strength. A higher sintering temperature for electrodes that are applied to our tubes is indicated. The electrodes, however, are highly porous and exhibit good conductivity.

5.2.5 Subtask D. Porous Support Tube Fabrication

Work has continued on producing in-house, extruded calcia-stabilized zirconia support tubes to desired specifications.

Introduction

A porous support tube fabrication process has been developed for calcia stabilized zirconia $(\text{ZrO}_2)_{0.85}(\text{CaO})_{0.15}$ powders. Tubes formed by extrusion with starting powders of 60 w/o of - 325 + 400 mesh: 40 w/o of - 400 + 500 mesh (Batch A) and 70 w/o of - 400 + 500 mesh: 30 w/o of - 500 mesh (Batch B) material have 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. Scanning electron micrographs indicate that the tube surface pores are in the range of 10-11 μm in diameter, with some irregularities caused by scoring of the surfaces by the extrusion die.

Process verification runs were completed to determine shrinkage factors and a new extrusion die assembly is in the process of fabrication in our machine shop. Negotiation with a potential outside vendor was not pursued during this quarter.

Experimental

Material preparation and tube fabrication powder preparation were limited to Batch B material of 70 w/o - 400 + 500: 30 w/o - 500 mesh material of Zircoa 8 w/o calcia-stabilized zirconia powders to determine reproducibility of the extrusion process. Other material batches are being held in readiness until the delivery of the redesigned extrusion die. This new die assembly was designed to accommodate a larger batch ($\sim 50\%$ increase) for extrusion and has part dimensional changes that should produce porous support tubes with ~ 0.040 inch (1000 μm) wall thickness.

The process procedure which consists of weighing, dry blending, kneading the mixture of powder fractions (with plasticizers, water and

wetting agent), was carried out before extrusion. Then the extruded tubes are dried in a humidity drying oven, fired in a presintering furnace (first firing) and finally fired in a gas pot furnace at 1800°C for two hours in a hanging position.

The support tubes that have been fabricated by this process have been characterized for their apparent porosity, shrinkage, tensile strength, and thermal expansion.

Results and Discussion

Since the experimental tubes fabricated from both Batches A and B did not show any marked changes in the physical properties during processing, verification runs used batches of B material to determine the shrinkage characteristics of $(\text{ZrO}_2)_{0.85}(\text{CaO})_{0.15}$ porous tubes.

Table I shows representative data of porous tubes fired at 1800°C for two hours. Lots B-11, B-12, and B-13 were selected because 63% of the tubes were straight after firing at 1800°C for two hours. The spread in the apparent porosity and shrinkage data is due mainly to the extrusion of small batches and space or clearance from the floor to the orifice of the exit end of the extruder. The extrusion process is sensitive to stop and go operations and frequent stops tend to increase variation in tube diameter and wall thickness.

The inherent brittleness of calcia stabilized zirconia tubes makes it difficult to obtain reliable strength data. Table II lists several test results of "tensile strengths" of the porous support tubes. Conventional tensile strength data of most ceramic materials have involved the well known flexure test^(6,7) as a means for evaluating tensile strengths. Taking the data from the three-point flexure test (MOR) the tubes have met the 5000 psi specification for tensile strength (Table II). Thermal expansion measurements taken on actual segments of porous support tubes shows an expansion characteristic of approximately 10×10^{-6} m/m/°C. Fig. 8 shows the expansion and cooling curves of a porous support tube fired at 1800°C for two hours. Figs. 9 and 10 are

TABLE I

Data Obtained On Porous Tubing Made By Extrusion,
Using Powder Supplied By Zircoa

Batch B

70 w/o - 400 + 500 mesh
30 w/o - 500 mesh

	<u>B-11</u>	<u>B-12</u>	<u>B-13</u>
Diameter O.D. (in.)	0.506-0.512	0.496-0.505	0.499-0.513
Diameter I.D. (in.)	0.373-0.378	0.350-0.370	0.357-3.89
Bulk Density (g/cm ³)	3.56	3.34	3.21
Apparent Porosity	31.02%	33.25%	35.00%
Specific Gravity	5.16	5.01	4.95
Shrinkage Height	(Total shrinkage from green to fired state)		
Height	5.20%	6.21	5.99%
Diameter	5.21%	5.16	5.21%

Tubes fired at 1800°C for two hours.

TABLE II

Fired Properties of Extruded Porous Calcia-Stabilized
Zirconia Tubes - In-House Development

	<u>Flexure Test (Tensile)</u>
Three-point flexure	5550 psi
Four-point flexure	4350 psi
Tensile Strength	
Set A	1650 psi
Set B	2447 psi

The above results are averages of three specimens.

Fig. 8 — Thermal expansion of porous calcia stabilized zirconia tube - sample B-11

180 X

55 μm = 1 cm

450 X

22 μm = 1 cm

Fig. 9 Interior Surface of Extruded Calcia-Stabilized Zirconia Tubes - In-house Development.

55 μm = 1 cm

22 μm = 1 cm

Fig. 10 Exterior Surface of Extruded Calcia Stabilized Zirconia Tubes - In-house Development.

SEM photographs of the interior and exterior surfaces of an extruded porous support tube. The surfaces are relatively free from "debris", as compared to cast porous support tubes.

5.3 TASK 3. COMPONENT TESTING

The purpose of this task is to test selected component materials identified in Task 1 and meeting the fabrication requirements of Task 2, using a test sample and testing mode that most meaningfully evaluates each individual component of interest.

5.3.1 Subtask 3A. Interconnection Testing

Measurements of interconnection material resistivity alone, by means of thin film specimens with lateral current flow, were deferred in order to concentrate on the new crossed-electrode method for combination testing, discussed in the next section.

5.3.2 Subtask 3B. Combination Testing

Combination testing involves at least two adjacent fuel cell components (for example, interconnection or electrolyte film plus fuel or air electrode) and is carried out with the current flow perpendicular to the plane of the interconnection or electrolyte film, just as it will occur in an operating fuel cell. For good interconnection or electrolyte materials at 1000°C, the resistance of the film itself is very low, on the order of milliohms, so that interface resistances between the components may become important. Some of the more common sources of interface resistance might be: (1) a chemical reaction layer at the component interface, (2) cracking or separation between the components and (3) spreading resistance, arising from multi-point contact between components.

5.3.2.1 Crossed-Electrode (CE) Method for Measuring Combination Specimen Resistance

Due to the inherently-low resistance of combination specimens, it is essential to: (a) enhance the specimen resistance by employing a very small specimen area, and (b) eliminate or minimize the resistance

of electrode leads and their contacts with the electrodes. The Crossed-Electrode (CE) method for measuring combination specimens, discussed in a previous report, ⁽⁸⁾ meets these requirements well. It is shown schematically in Fig. 11. The active combination specimen area is only where the electrodes cross, which satisfies requirement (a). Requirement (b) is satisfied by employing a four-terminal resistance measurement, with the extensions of the current electrodes serving as potential electrodes. The ultimate limitation in the CE method begins to appear when the specimen resistance is low enough to be comparable with the lateral resistance of the electrodes in direct contact with the specimen. At this point, a lateral potential drop occurs across the electrode which causes the apparent resistance of the specimen (as measured by the four-terminal method) to appear lower than the true specimen resistance. An analysis of this effect has been carried out which enables one to correct for it, or better still, to choose an electrode width and thickness for which the effect will be small. It was found* that

$$R_a = \frac{\sqrt{R_e R_t}}{\sinh \sqrt{R_e / R_t}}$$

or approximately

$$R_a \approx R_t - \frac{1}{6} R_e \text{ for } R_t > R_e$$

where

R_a = apparent specimen resistance

R_t = true specimen resistance

R_e = lateral (sheet) resistance of both electrodes

$$= 2 \rho_e / \delta_e$$

with ρ_e = resistivity of electrode material

δ_e = thickness of electrode

*A distributed parameter treatment of the problem was used which was similar to that discussed in the first annual report.

Fig. 11A — Schematic of crossed-rod method for measuring electrical contact resistance

Fig. 11B — Schematic of crossed-electrode geometry for combination testing

A convenient form of the results for the purpose of correcting experimental data appears in the graph of Fig. 12.

Examination of the approximate equation above shows that there are two ways in which the relative size of the effect can be reduced: (1) reduce the lateral electrode resistance by using thicker electrodes and (2) increase the specimen resistance by decreasing its area; i.e., by decreasing the electrode width.

5.3.2.2 Experimental Test of the CE Method on a Thin Film $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ Specimen

The details of the CE specimen geometry were given in the Sixth Quarterly Report.⁽⁸⁾ A photograph of the specimen mounted in the measurement apparatus is shown in Fig. 13. Briefly, it consisted of an alumina substrate, sputtered platinum electrodes, approximately 0.16 cm wide and 5 microns thick, and an interconnection film consisting of $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$, 18 microns thick, sputtered on the substrate at 350°C. For this initial test of the CE method, platinum was chosen as the electrode material, to permit measuring the specimen both in air and hydrogen-water atmospheres.

Measurements were carried out from 65°C up to 1000°C. The current density employed was usually 40 mA/cm² (1 mA through a specimen area of 0.025 cm²); however, at 800 and 1000°C, measurements were made at both 40 and 400 mA/cm². The apparent specimen resistances ranged from 8000 to 0.031 ohms. Platinum electrode sheet resistances ranged from 0.047 to 0.145 ohms.

A graph of the CE resistance data as a function of temperature is presented in Fig. 14. It was decided that for present comparison purposes, it would be more convenient to plot an "effective specimen resistivity", rather than actual specimen resistance. This enables one to quickly compare these results with previous data (see the Fifth Quarterly Report) for this same material. Several aspects of the CE data are worthy of comment. First, one notes that the data for the hydrogen-water atmosphere agree well with previous results, with the

Curve 693468-A

Fig. 12-Correction for the apparent specimen resistance, R_a , when it becomes comparable to the lateral electrode resistance, R_e , in a crossed-electrode measurement.

Fig. 13. Crossed-electrode thin film specimen of $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$, mounted in measurement apparatus. (Substrate size, 1 in. x 1/2 in.)

Fig. 14—Effective specimen resistance vs temperature for a crossed-electrode specimen of $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$

exception of the highest temperature point. Second, it is evident that the data for the air atmosphere are noticeably higher in magnitude and slope than previous results. It is possible, then, that a significant (but not prohibitively large) interface resistance is occurring in this specimen situation. Third, although at 800 and 1000°C, the specimen current density was varied (40 mA/cm^2 , 400 mA/cm^2), no effect whatsoever on specimen resistance was seen. At this time, we cannot suggest a mechanism which will account for these results; however, we feel that the difference in behavior for the two atmospheres may be significant. It is essential to note that the interface behavior should depend strongly on the electrode material. Platinum was chosen as a convenience in these first tests. Future combination specimens will employ nickel or tin-doped indium oxide electrodes, which correspond, more realistically, to the actual fuel cell situation.

From our initial tests of the crossed-electrode (CE) method for combination specimen testing we conclude the following.

- 1) The CE method greatly reduces lead and contact resistance problems, enabling one to measure combination specimens with resistances in the milliohm range.
- 2) An analysis of the CE method indicates that additional improvements can be made by changing the electrode width and thickness.
- 3) The results of measurements on a combination specimen, consisting of an interconnection film with platinum electrodes, suggests that significant interface resistances were present in an air atmosphere.
- 4) No dependence on current density was observed in an air atmosphere.

5.3.2.3 Useful Life Testing

Work in this area is presently awaiting refinement of the EVD process for preparing interconnection films. Meanwhile, new masking tape materials, useful at 1300°C, are being identified, so that they can be used in cell fabrication. Also fuel electrodes have been deposited on in-house tubing and will be used in cell and 3-cell stack fabrication.

5.4 TASK 4. ALTERNATE ELECTROLYTE AND BATTERY DESIGNS

Work in this area consists of:

- 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 the existing cell and cell stack design, if test results indicate problems, particularly, with respect to mechanical over-stressing of cell or cell stack component(s).

With regard to (1), close liaison is maintained with personnel at Brookhaven National Laboratories, at the National Bureau of Standards, and at the Montana Energy and MHD Research and Development Institute (all members with Westinghouse on the DOE, Solid Oxide Electrolyte Coordinating Committee), with regard to any new developments in this area. Also, interaction at national meetings and in private conversations with other professionals working on solid oxide electrolytes, has and will continue to occur, to insure that promising candidates, other than our present yttria-stabilized zirconia solid oxide electrolyte, will not be overlooked.

Alternate cell and stack designs, referred to in (2), will be evaluated, only if problems to the present Westinghouse design, using the best component materials that have been identified, are detected.

6.0 SUMMARY OF FUTURE PLANS

The following work plans are projected for the eighth quarter of the program.

Task 1. Materials Identification and Selection

Subtask A. Interconnection Literature Search

Work was completed on this task in the second quarter.

Subtask B. Interconnection Materials Development

The effect of preparation differences on oxygen uptake and diffusion rate into lanthanum chromite interconnection materials will be studied, to determine possible problems with oxygen leakage through the interconnection.

Stability of the solid solution of Mg^{2+} in $La_{0.95}Mg_{0.05}Cr_{0.75}Al_{0.25}O_3$ will be investigated in view of possible local strains which might be caused by formation of a second phase component in the interconnection film.

RF sputtered interconnection films will be deposited from hot pressed target materials, to determine if its quality can be improved over that obtained by using powder target material.

Subtask C. Development of Other Stack Components

Work here will actually be concentrated on the fabrication techniques and the films produced by these techniques. The best film techniques will be used in the construction of unit cells and small cells for test evaluation. The air, fuel, electrolyte and support tube materials have been identified.

Task 2. Fabrication Techniques

Subtask A. Interconnection

Work continues to refine the EVD process to produce suitable films of modified lanthanum chromite in porous nickel cermet fuel electrodes (on porous zirconia support tubes). When deposited at proper composition, thickness and resistance, the technique will be used in preparing unit cells and small stacks for test evaluation.

Subtask B. Electrolyte

The developed EVD process will be used to produce the yttria-stabilized zirconia films in the construction of multi-component, combination tests, as well as unit cells and cell stacks.

Subtask C. Air and Fuel Electrodes

With regard to the air electrode, a simple technique to provide uniform distribution and adherence of the seed grains on the substrate before its exposure to the vapor stream of the reactants of the deposition reaction should be devised. Such a technique will facilitate the testing of the influence of the seed grains on the final film texture.

The cause for the creation of porous film bands of air electrode current collector should be investigated. It may provide the necessary information for the proper modification in the reactor design features that will result in the formation of uniform porous films.

Other changes in the CVD-parameters, such as the rate of supply of the reactant vapors to the deposition zone, may also be important to the air electrode film texture.

Fuel electrode fabrication onto support tubes will continue, to obtain desired porous structures that will enable construction of unit and small cell stacks to proceed.

Subtask D. Porous Support Tube

Material preparation and an extrusion fabrication process to produce porous calcia-stabilized zirconia tubes have been developed.

A new extrusion die assembly has been designed and is in the process of fabrication in our machine shop. This die will be used to produce uniform tubes of proper wall thickness for use in unit cell and small cell stack construction and testing.

Task 3. Component Testing

Subtask A. Interconnection

Thin film resistivity measurements will be made on strontium-doped lanthanum chromite. The effect of oxidizing and reducing atmospheres on this material (in thin film form) will be determined.

Subtask B. Combinations

Combination specimens consisting of interconnection films plus nickel or tin-doped indium oxide electrodes will be prepared in crossed-electrode configuration. Tests will be carried out to determine if significant interface resistances occur for these combinations, which will exist in the actual fuel cell.

Subtask C. Useful Life Testing

Effort is being concentrated on fabricating the interconnection material to the desired rare earth chromite composition in the EVD deposited films. This effort is necessary to permit construction of unit cells to proceed. These unit cells will be prepared and evaluated toward obtaining target performance and life objectives, to attain Milestone 4 on the program.

Task 4. Alternate Electrolytes and Battery Designs

Literature follow and direct contact with professionals working on electrolytes will continue.

Cell and stack designs will await results of tests on presently-established unit cell designs, incorporating newly developed component materials and fabrication techniques.

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- D. F. Bradley - Interconnection Fabricating by EVD
- J. B. McNally - Porous Support Tube
- G. M. Halgus - Porous Support Tube
- E. Diaz - Porous Support Tube
- G. J. Mowry - Porous Support Tube
- J. Valentich - Porous Support Tube Evaluation
- F. Fidler - Porous Support Tube

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7. Edited by J. B. Wachtman, Jr., "Mechanical and Thermal Properties of Ceramics Proceedings of a Symposium, 1968, National Bureau of Standards Special Publication 303, Issued May 1969. A. L. Mordfin and M. J. Kerper, Strength Testing of Ceramics - A Survey, pp. 243.
8. Thin Film Battery/Fuel Cell Power Generating System, Fifth Quarter Report (for the period April 1977 - June 1977) ERDA Contract C-1197-6, July 18, 1977, pp. 55-56.

9.0 PERMANENT RECORD BOOK ENTRIES

Figuring Books, containing information described in this report are:

207773	pp. 57-65
207906	57-58, 60-67
208043	47-49, 65-77
208037	9-19
208023	25-34
207905	86-103