C-1197-7

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Contract

Thin Film Battery/Fuel Cell Power Generating System

Sixth Quarter Report

Task E2

Project Status Report for the

Period July 1977 - September 1977

W. Feduska, Project Manager

A. O. Isenberg, Technical Coordinator

J. E. Bauerle, W. J. Biter, Y. Ichikawa,

R. J. Ruka, L. N. Yannopoulos, Contributors

MASTER

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Research and Development Center
WESTINGHOUSE ELECTRIC CORPORATION
Pittsburgh, Pennsylvania 15235

October 7, 1977

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TABLE OF CONTENTS

	<u>Page</u>
1.0 Abstract	vi
2.0 Introduction	1
3.0 Technical Background	2
4.0 The Present Program	3
5.0 Overall Technical Effort	5
5.1 Task 1. Material Identification and Selection	5
5.1.1 Subtask 1A. Interconnection Literature Search	5
5.1.2 Subtask 1B. Selection of Interconnection Materials	5
5.1.2.1 Oxygen Content of $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_{3-x}$	6
5.1.2.2 Examination of $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ for Possible Minor Phase Constituents	9
5.1.2.3 Scanning Electron Microscope (SEM) Examination of RF Sputtered $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$	12
5.1.2.4 Summary	13
5.1.3 Subtask 1C. Development of Other Stack Components	16
5.1.3.1 Fuel Electrode Development	16
5.1.3.2 Air Electrode Development	17
5.1.3.3 Solid Oxide Electrode Development	17
5.2 Task 2. Fabrication Techniques	17
5.2.1 Subtask 2A. Interconnection Fabrication	17
5.2.1.1 RF Sputtering of Interconnection Material	18
5.2.1.1.1 Sample Preparation	18
5.2.1.1.2 Equipment	19

TABLE OF CONTENTS (Cont)

	<u>Page</u>
5.2.1.1.3 Summary of Film Depositions	19
5.2.1.2 Fabrication of Interconnection Films by Electrochemical Vapor Deposition (EVD)	21
5.2.1.2.1 Characterization of Lanth- anum Chromite EVD Films	24
5.2.1.2.2 Summary of Work Regarding EVD of Modified Lanthanum Chromite	27
5.2.2 Subtask 2B. Fabrication of Solid Oxide Electrolyte	28
5.2.3 Subtask 2C. Air Electrode Fabrication	28
5.2.3.1 Summary	37
5.2.4 Subtask 2C. Fuel Electrode Fabrication	38
5.2.5 Subtask 2D. Porous Support Tube Fabrication	40
5.2.5.1 Powder Preparation	42
5.2.5.2 Paste Preparation	42
5.2.5.3 Forming and Densification	43
5.2.5.4 Results and Discussion	46
5.2.5.5 Summary	46
5.3 Task 3. Component Testing	46
5.3.1 Subtask 3A. Interconnection Testing	50
5.3.2 Subtask 3B. Combination Testing	50
5.3.2.1 Two-Contact Measurement on a $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ Specimen	50
5.3.2.2 Preparation of Crossed-Electrode Specimens	52
5.4 Task 4. Alternate Electrolyte and Battery Designs	55
5.5 Vapor Transport Studies of Indium Oxide and Interconnection	55
6.0 Summary of Future Plans	57
7.0 References	60
8.0 Permanent Record Book Entries	63

LIST OF ILLUSTRATIONS

	<u>Page</u>
1. Experimental Setup for Measuring Weight Changes at 1000°C of Lanthanum Chromites	8
2. Oxygen Loss from $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_{3-x}$ at 1000°C in Controlled Atmosphere Microweighing System	10
3. $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ Film-RF Sputtered onto 225°C Al_2O_3 Substrate	14
4. $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ Film-RF Sputtered onto 525°C Al_2O_3 Substrate	15
5. Reactor Arrangement for EVD of Sr-doped LaCrO_3 Interconnection Films at Temperatures above 1200°C	23
6. Arrangement of Substrate Tube and Holder for EVD of Electrolyte and Interconnection Oxide Films	25
7. Lanthanum Chromite EVD Films on Nickel Electrode	26
8. Resistivity Profile of CVD Tin-Doped Indium Oxide Films on Ceramic Target Tubes	29
9. Resistivity per Unit Thickness vs Temperature of Tin-Doped Indium Oxide Film in Alumina Tube (Run IN _{II} -1)	31
10. Resistivity per Unit Thickness vs Temperature of Tin-Doped Indium Oxide Film on Zirconia Tubes	32
11. Resistivity per Unit Thickness vs Temperature of Tin-Doped Indium Oxide Film on Calcia-Stabilized Zirconia Tubes Supplied by ZIRCOA	33
12. Micrograph Showing the Type of Film Obtained from CVD Experiments IN _{II} -1 and IN _{II} -4	36

LIST OF ILLUSTRATIONS (Cont)

	<u>Page</u>
13. Arrangement for Nickel Plating of Fuel Electrodes	39
14. Fuel Electrode Resistance Changes with Temperature and Reduction of Resistance by Electroplating	41
15. MSA Sedimentation Particle Size Analysis of Zircoa 8 w/o Calcia-Stabilized Zirconia	44
16. MSA Sedimentation Particle Size Analysis of Zircoa 8 w/o Calcia-Stabilized Zirconia	45
17. Exterior Surfaces of 8 w/o Calcia-Stabilized Zirconia Tubes from Zircoa	48
18. Interior Surface of 8 w/o Calcia-Stabilized Zirconia Tubes from Zircoa	49
19. Tubular Combination Specimen with Contacts for Two- or Three-Electrode Measurements	51
20. Resistivity vs Temperature for a Tubular Combination Specimen	53
21. Test Specimen for Evaluation of Crossed-Electrode Technique for Measuring Low Resistance Interconnection Films	54

LIST OF TABLES

	<u>Page</u>
1. Summary of RF Sputtered $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ Films	20
2. Film Thickness Resistivity and Chemical Analysis Data of As-Prepared Films	35
3. Data of Tubing Made by Extrusion, Using Powder Supplied by Zircoa	47
4. Data of Tubing Supplied by Zircoa	47

1.0 ABSTRACT

During the sixth quarter, development work continued on the interconnection material, on the air electrode current collector, on the fuel electrode, on the porous support tube and on the electrochemical vapor deposition (EVD) process for preparation of interconnection films of rare earth chromites.

In particular, an evaluation of the oxygen content in $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_{3-x}$ was initiated, to assist in determining the effect of oxygen depletion (oxygen vacancy formation) in the compound on oxygen ion transport through the fuel cell interconnection. Also, investigation of this same interconnection material is proceeding to determine whether or not minor phases are present and their effects on expansion, conductivity and overall stability, under operating conditions. Second phases have not, to date, been detected, in tests using powder x-ray diffraction for high purity starting materials or in micrographic SEM examinations of films.

Examination of $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ films formed by RF sputtering indicate that mechanically sound films stable to post-sputtering heat treatment in either air or hydrogen water atmospheres can be made if the sputtering is made at substrate temperatures above about 500°C. EVD films that are mechanically sound and chemically stable in air have been made, but the alkaline earth substituent, necessary to obtain sufficient electrical conductivity, was not incorporated in the film under the conditions used. EVD conditions will be adjusted to overcome this problem, which is delaying the preparation of unit cells and their testing.

The composition presumed to be very nearly $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ at 1000°C in air changes to about $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_{2.99}$ at an

equivalent open circuit fuel cell voltage of 1 volt. This small deviation from stoichiometry is expected to result in a small, but tolerable, oxygen leak rate across an interconnection film.

Air electrode current collector, tin-doped indium oxide films are being produced by chemical vapor deposition (CVD), with uniform thickness over about 10 inches of tube length. Characterization of these films shows that they have uniform composition upon continuous use of the starting reactant oxide material in the CVD-process. Desired film thickness (20-50 μm) and resistivity values ($\leq 10^{-3} \Omega\text{-cm}$) are being achieved. Work is proceeding to deposit the films on solid oxide electrolyte and interconnection films, as substrates.

Forming and densification of particle size fraction with a p/s ratio of 2.33 by extrusion and firing to 1800°C produced support tubes with porosity in the 31-34 percent range. Work is continuing to optimize the p/s ratio of the particle size fractions, using in-house starting materials. Meanwhile, negotiations with a second commercial supplier have been initiated for a limited quantity of materials and support tubes.

Measurements are continuing on tubular combination specimens with EVD-deposited interconnection films. The cross-electrode specimens are being prepared and will be tested and the technique evaluated for application to combination test specimens and complete cells. Resistivity measurements on thin film specimens are continuing.

Vapor transport studies have been initiated on indium oxide and lanthanum chromite and will continue, but data obtained to date is inconclusive.

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 a basic fuel, conversion efficiencies of over 50% are possible, if the fuel cell is integrated with a coal gasification process in order to provide necessary heat for the endothermic process.

The high-temperature solid-electrolyte fuel cell operates at 1000°C without expensive catalysts, on a carbon monoxide-hydrogen gas mixture, provided by the gasification of coal. 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:

- 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 and 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 ERDA 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 ERDA 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, had not exceeded 100 hours*. 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⁾

*F. J. Rohr, of Brown, Boveri & Cie AG, described at the "High-Temperature Solid Oxide Fuel Cells" Workshop at Brookhaven National Laboratories in May 1977 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.

4.0 THE PRESENT PROGRAM

The purpose of this two-year, ERDA-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 also will 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.

*Formerly E(04-3)-1197).

The culmination of all efforts on the 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) incell 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 particularly lanthanum chromite, has been selected for more intensive investigation to produce a satisfactory interconnection material.

5.1.2 Subtask 1B. Selection of Interconnection Materials

The properties of lanthanum chromite can be altered by additives which replace part of either the lanthanum or chromium. These

composition changes can be made to increase the conductivity, to eliminate a phase change occurring below about 270°C and to adjust the thermal expansion. With these properties improved, lanthanum chromite is a strong candidate to satisfy the stringent requirements for an interconnection material to be used with the thin layer, zirconia electrolyte fuel cell.

Different additives change, to a different degree, other important properties of the interconnection oxide, such as: (1) ionic conduction (small but significant), (2) the ease of fabrication (as dense layers of well defined composition) and (3) the volatility of the chromium component. In the course of this development, it will be necessary to adjust the concentration and type of additives to optimize the properties, particularly with respect to alterations which will aid the fabrication processes. In particular, the electrochemical vapor deposition (EVD) fabrication technique is sensitive to the level of conductivity due to the small ionic component.

5.1.2.1 Oxygen Content of $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_{3-x}$

In the ideal perovskite crystal structure, ABO_3 , large metal ions in the A sites are coordinated to twelve oxygen nearest neighbors, and smaller metal ions in the B sites to six oxygen nearest neighbors. In reality, most perovskite-like crystal structures, such as the substituted lanthanum chromite interconnection materials of current interest, deviate to different degrees from this ideal crystalline arrangement. Typical deviations take the form of unequal displacements of the oxygens about the A (lanthanum) positions and the presence of vacancies at either the oxygen or metal ion sites. In addition, variations of the electronic structure, such as positive holes associated with the B (chromium) sites, also occur as a function of the type and degree of doping with other chemical constituents.

As an example, in $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3$, divalent strontium substitutes for part of the large La^{3+} ion at A sites. Charge compensation is provided by electron holes at the B (chromium) sites at high oxygen

pressures (e.g., air at atmospheric pressure). However, at low oxygen partial pressures, corresponding to the fuel side of a fuel cell, another mechanism for charge compensation comes into play, namely, the loss of oxygen ions from the lattice. For each O^{2-} lost, a lattice vacancy is left at a normal oxygen ion site and two electron holes are eliminated. This is indicated by the following formula:

In this formulation Cr^{4+} represents a chromium ion plus a localized positive hole, $O^{\square}$ represents an oxygen vacancy, and x is the number of oxygen vacancies per mole of the formula, as written.

Similar types of charge compensation and oxygen loss occur if the alkaline earth substituent is magnesium instead of strontium. However, in this case, it has been argued that the magnesium ion is closer in size to the chromium and may thus reside on the B rather than the large A (lanthanum) type sites of the perovskite crystal. In either event, loss of at least a small quantity of oxygen from the crystal lattice and the presence of oxygen vacancies may be expected at the low effective oxygen partial pressures encountered in fuel atmospheres.

Since the presence of oxygen vacancies is expected to result in some degree of oxygen ion transport through the fuel cell interconnection, a measurement of the variation in oxygen content with fuel or oxygen containing (e.g., air) atmospheres is desirable to help study the magnitude of this undesirable effect. (A more detailed discussion of the conduction mechanism of modified lanthanum chromite will follow in the next report.)

To study oxygen concentration changes, we assembled a controlled, flowing gas atmosphere, micro-weighing system illustrated schematically in Fig. 1. In this system, a sample bar of the interconnection oxide is located in the high temperature ($\sim 1000^{\circ}C$) furnace zone by attachment to a platinum wire suspended from the beam of a microbalance, which is located in a cool section of the apparatus. Near the sample is

Fig. 1. Experimental Setup for Measuring Weight Changes at 1000°C of Lanthanum Chromites in Wet Air and Water/Hydrogen Mixtures

placed a cell made up of a zirconia electrolyte and platinum electrodes, to measure the oxygen chemical potential of the flowing fuel (H_2/H_2O) or oxygen-containing atmospheres to which the sample is to be exposed. The cell voltage is that which would be obtained as the open circuit voltage of a corresponding zirconia-electrolyte fuel cell with the given gas atmosphere. The oxygen monitoring cell^{2,3} may be written:

Fig. 2 shows a weight difference corresponding to the loss of less than 0.3% of the oxygen content of the sample going from the most oxidizing (0.24 volt) to the fuel rich (1 volt) condition. The additional weight change between 0.24 volts and 0 volts (air) is not shown here but is very small. If the $La_{0.95}Mg_{0.05}Cr_{0.75}Al_{0.25}O_{3-x}$ sample contains nearly the stoichiometric amount of oxygen (x nearly 0) in an air atmosphere, these results indicate that the composition in the fuel atmosphere (at 1 volt) may be written $La_{0.95}Mg_{0.05}Cr_{0.75}Al_{0.25}O_{2.99}$. A relatively small oxygen leak via oxygen vacancies through the interconnection is thus indicated. The magnitude of the leak must ultimately be determined experimentally in an actual cell or stack configuration. It will depend on the diffusivity and concentration profile of the oxygen vacancies across the interconnection and surface blocking effects which reduce gaseous diffusion to and from the electrode interface areas.

The small oxygen deficit found in the doped lanthanum chromite in fuel atmospheres is expected to be dependent on the type and concentration of the alkaline earth constituent, as indicated by differences shown in earlier microweighing measurements at room temperature of samples of both $La_{0.84}Sr_{0.16}CrO_{3-x}$ and $La_{0.95}Mg_{0.05}Cr_{0.75}Al_{0.25}O_{3-x}$ quenched from 1000°C.

5.1.2.2 Examination of $La_{0.95}Mg_{0.05}Cr_{0.75}Al_{0.25}O_3$ for Possible Minor Phase Constituents

Not only do oxygen vacancies appear to exist in these systems, but other defects, such as cation vacancies and interstitials, might

Fig. 2 - Oxygen Loss from $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_{3-x}$ at 1000°C in Controlled Atmosphere Microweighing System

also occur in the perovskite-like ABO_3 crystal structure. For example, Anderson⁽⁴⁾ suggests that his experimental data on the difference in phase change temperature in magnesium-doped lanthanum chromites support the premise that divalent magnesium ions do not exist at normal La^{3+} sites in materials mixed to give the empirical formulations written in this report as $La_{0.95}Mg_{0.05}CrO_3$ or $La_{0.95}Mg_{0.05}Cr_{0.75}Al_{0.25}O_3$. In these formulations it seems likely that all the La^{3+} would be accommodated in the large (A) sites of the perovskite structure. However, the magnesium ion has several possible options for its location; e.g., it might (1) displace part of the chromium from the small B sites, (2) occur as a second phase, such as $MgCr_2O_4$ or MgO , (3) occupy part of the large B sites, (4) occupy interstitial positions with or without the presence of vacancies at the large A sites, and (5) some combination of these.

Magnesium-doped lanthanum chromite has a higher conductivity than the undoped material and is said to have p-type conductivity. This implies that at least part of the Mg^{2+} has entered the lattice by displacing either Cr^{3+} at the small B sites of the ABO_3 perovskite structure or occupies the large B sites along with La^{3+} . If, e.g., components are mixed together to give a single or multi-phase composition with the empirical composition $La_{0.95}Mg_{0.05}Cr_{0.75}Al_{0.25}O_3$, and if Mg^{2+} cannot enter the La^{3+} type sites because of size discrepancies, there is a possibility that a small quantity of a second phase, perhaps $Mg_2Cr_2O_4$, Cr_2O_3 , or MgO will be present. Thus far we have not detected second phase components micrographically in sputtered and annealed films. The problem is further complicated by the difficulty of obtaining sufficiently precise analytical data for all components of the different lanthanum chromite compositions. However, small amounts of $MgCr_2O_4$ have been found⁽⁵⁾ in commercial " $La_{0.95}Mg_{0.05}CrO_3$ ", although exact composition and homogeneity of the materials are in question in this instance.

Thus far our X-ray diffraction evidence, using filtered x-radiation on $La_{0.95}Mg_{0.05}Cr_{0.75}Al_{0.25}O_3$ prepared from high purity oxides, pressed, sintered and ground four times to react and homogenize,

has not revealed a second phase. However, X-ray diffraction using monochromatic radiation can sometimes detect a fraction of a percent of a trace phase and we have therefore reexamined the specimens with this more sensitive technique.

The materials checked were (1) $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$, (2) $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3$ and (3) $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3 + 0.025 \text{MgCr}_2\text{O}_4 + 0.025 \text{MgO}$. No second phases were detected in (1) or (2), while in the mixture (3) MgCr_2O_4 , intentionally introduced to check the detection limits of the method, was easily detectable but the MgO was not. Since the materials were prepared by successively grinding, pelleting, and sintering at 1500-1600°C four times in covered alumina boats, it would seem that any MgCr_2O_4 which might have formed would be highly crystalline and detectable. However, loss of chromium by evaporation could account for the absence of a detectable MgCr_2O_4 or Cr_2O_3 phase while small quantities of unreacted MgO are not detectable in our tests. Thus, the whereabouts of the Mg^{2+} in $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ is still uncertain. Hopefully, any undetected second phases that could possibly be present will not be such as to affect the mechanical or chemical properties of interconnections made of this type of material.

5.1.2.3 Scanning Electron Microscope (SEM) Examination of RF Sputtered $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$

The previous report⁽⁶⁾ presented evidence based on scanning electron microscope (SEM) pictures, that films of $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ interconnection material, formed by RF sputtering on nickel electrodes or alumina substrates held at 200-300°C during the sputtering process, showed cracks after annealing at 1000°C in a water-hydrogen (fuel) atmosphere. In contrast, similar films deposited on alumina and heated in dry or wet air did not crack. These films appeared amorphous to X-ray diffraction, as sputtered, but became highly crystalline after a 1000°C anneal for 3 hours. Subsequent anneals in water-hydrogen did not crack these films. This behavior suggested that the cracking damage by the water-hydrogen atmosphere occurred only during the recrystallization

process. Therefore, in this quarter films were sputtered onto heated substrates at temperatures where appreciable crystallization occurred during the sputtering process, to see if this cracking difficulty could be eliminated.

Fig. 3 shows a film sputtered at the relatively low substrate temperature of 225°C onto alumina. As before, the film cracked only when subjected to the water-hydrogen anneal. Fig. 4 shows a film sputtered at the higher alumina substrate temperature of 525°C where appreciable crystallization of the film occurs. It is seen that the film did not crack in this instance in the water-hydrogen atmosphere anneal at 1000°C.

We may conclude from these data that we need the high substrate temperatures, or perhaps a different high temperature heat treatment schedule, if an anneal in water-hydrogen atmospheres is to be used. The water-hydrogen atmosphere is useful in preventing oxidation of the nickel in a nickel electrode/interconnection film during the post-sputtering heat treatment. Other possibilities for preventing the cracking might be reducing the amount of hydrogen in the annealing atmosphere or substituting a CO/CO₂ mixture for the H₂/H₂O as the protective atmosphere.

We may infer from these data and the data of Section 5.2.1, that mechanically sound interconnection films can be made by either the RF sputtering or the EVD processes. However, the EVD process must be altered to incorporate an alkaline earth component, such as Sr²⁺ or Mg²⁺, to obtain suitable conductivity properties.

5.1.2.4 Summary

Examination of La_{0.95}Mg_{0.05}Cr_{0.75}Al_{0.25}O₃ films formed by RF sputtering indicate that mechanically sound films stable to post-sputtering heat treatment in either air or hydrogen/water atmospheres can be made if the sputtering is done at substrate temperatures above about 500°C. EVD films that are mechanically sound and chemically

1 2

20 micrometers

A. As Sputtered.

1 2

20 micrometers

B. Heated 3 hours in air at 1000°C.

1 2

20 micrometers

C. Heated 3 hours in H_2/H_2O at 1000°C.

Fig. 3. $La_{0.95}Mg_{0.05}Cr_{0.75}Al_{0.25}O_3$ Film--RF Sputtered Onto $225^\circ C$ Al_2O_3 Substrate

1. Al_2O_3 Substrate

2. $La_{0.95}Mg_{0.05}Cr_{0.75}Al_{0.25}O_3$ Film

1
2
20 micrometers
A. As sputtered.

1
2
20 micrometers
B. Heated 3 hours in air at 1000°C.

1
2
20 micrometers
C. Heated 3 hours in H_2/H_2O at 1000°C.

Fig. 4. $La_{0.95}Mg_{0.05}Cr_{0.75}Al_{0.25}O_3$ Film--RF Sputtered Onto $525^\circ C$ Al_2O_3 Substrate

1. Al_2O_3 Substrate
2. $La_{0.95}Mg_{0.05}Cr_{0.75}Al_{0.25}O_3$ Film

stable to air atmospheres have been made, but the alkaline earth substituent necessary to obtain sufficient electrical conductivity was not incorporated in the film under the conditions used.

The composition presumed to be very nearly $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ at 1000°C in air changes to about $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_{2.99}$ at an equivalent open circuit fuel cell voltage of 1 volt. This small deviation from stoichiometry is expected to result in only a small, but tolerable, oxygen leak rate across an interconnection film.

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.

A typical electrode has a resistance of 0.05 Ω /square at room temperature. The resistance increases to nearly 0.3 Ω /square at 1000°C. The electrode resistance of presently fabricated electrodes is considered to be too high, by a factor of three. However, the resistance can be lowered by three methods: a) by increasing surface loading, b) by increasing nickel content in cermet, c) by electroplating nickel onto the existing cermet structure.

To improve the conductivity of the fuel electrode, electroplating nickel onto the continuous nickel layer produced by sintering of the fuel electrode are presently being investigated and are reported in Section 5.2.4, Subtask 2C, Fuel Electrode Fabrication.

5.1.3.2 Air Electrode Development

Development work, to date, has placed emphasis on the fabrication of antimony-doped tin oxide and tin-doped indium oxide current collectors for the air electrode. Present efforts are aimed at fabrication of the tin-doped indium oxide current collector, primarily because this material has a thermal coefficient of expansion (9.23×10^{-6} m/m/°C at 1000°C) more favorably matching that of the zirconia support tube ($\sim 10 \times 10^{-6}$ m/m/°C at 1000°C) than the antimony-doped tin oxide ($\sim 5.0 \times 10^{-6}$ m/m/°C). Vapor transport studies on In_2O_3 have been initiated. The initial work in this area is presented in Section 5.5. This work is detailed in the fabrication tasks section of this report (Section 5.2.3, Subtask 2C).

5.1.3.3 Solid Oxide Electrolyte Development

Yttria-stabilized zirconia (~ 10 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, to optimize the fabrication of the electrodes and substrate components.

5.2.1 Subtask 2A. Interconnection Fabrication

Fabrication techniques that are being considered for the interconnection candidate materials include radio frequency (RF) sputtering and electrochemical vapor deposition (EVD).

5.2.1.1 RF Sputtering of Interconnection Material

Results from the sputtering deposition of films of mixed oxide materials have been encouraging and have indicated the direction for improvement. In general, this is toward a higher substrate temperature, which seems desirable for a number of reasons - denser, more conductive films, for example.

5.2.1.1.1 Sample Preparation

Deposition of the interconnection material, $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$, is accomplished by RF sputtering and good quality films are obtained. Layers are being routinely deposited onto both alumina and zirconia substrates. Some problems were encountered in the deposition onto the porous zirconia, which now seem to be resolved. The films deposited onto zirconia had a poor appearance and seem to lack adhesion compared to the films on alumina substrates. The film came off the substrate as a powder when scraped. This is contrasted to the films deposited on alumina in the same deposition which would have a "smooth" appearing surface and usually "flake" off the substrate when scraped. This indicates the weakest point of this structure is the alumina/lanthanum chromite interface with the $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ layer itself having a high degree of integrity. With both types of substrate, however, the adhesion to the substrate was quite good. Application of the "scotch tape" peel test removed little or no material. This test consists of pressing a piece of adhesive tape to the film, removing it and examining the amount of material removed. As mentioned, most of these sputtered films tested in this manner indicated very good adhesion.

A number of approaches were taken to eliminate this "powdery" appearance of the films deposited onto the ZrO_2 . The first attempt was to electrically isolate the zirconia on the possibility that an electrochemical reaction was occurring between the plasma and the zirconia. This would occur on the zirconia and not the alumina, due to the higher conductivity of the zirconia at elevated temperature. The substrates

were electrically isolated by mounting them onto a small piece of alumina and holding them with quartz plates. This seemed to improve the film somewhat, but to an insufficient degree.

The most likely cause appears to be contamination of the substrates. This cause is alleviated by a 12 h, 1000°C air-heating of the substrates. Following the heating, the samples are stored in a dry atmosphere. After being loaded into the vacuum system, and immediately prior to the start of the deposition, they are pre-heated to 600°C. This treatment seems to be effective for removing any organic or volatile contamination and also any adsorbed gases trapped in this porous structure.

5.2.1.1.2 Equipment

As reported in the Fifth Quarterly report,⁽⁷⁾ the depositions done at higher temperatures for longer times were introducing a severe heat load into the system. The addition of a water-cooled baffle surrounding the substrate and sputter head solved this problem. During Run No. 19 insufficient water flow led to failure of a solder joint on the sputter head and caused water release into the vacuum system. This accident required an overhaul of the vacuum system, including the diffusion pump and mechanical pump. This was completed and an interlock installed which senses the temperature of the shield. When this temperature rises above 100°C the heating system is turned off.

The present substrate heater assembly was designed for flat substrates. To cover a tube will require a rotating substrate holder. This is being designed and will have a radiant heater positioned behind the tube.

5.2.1.1.3 Summary of Film Depositions

Table 1 summarizes the depositions from Run No. 17 to Run No. 24, the most recent run. The most significant change made in this series was the addition of oxygen during the sputtering. The deposited

TABLE 1

Summary of RF Sputtered $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ Films

Run No.	Samples	RF Power Input	Substrate Temperature	Ambient	Time	Comment(s)
17	Al_2O_3 (1) ZrO_2 (1)	350 W	450°C	Argon	7 hr	Thin run - Target surface turned green. Nonuniformity in samples appear related to nonuniformities in target material
18	Al_2O_3 (1) ZrO_2 (2)	350 W	525°C	Argon	15 hr	Thin ($<8\mu$). Severe flaking of Al_2O_3 .
19	LOST WATER COOLING					
20a	ZrO_2 (1) Al_2O_3	350 W	525°C	Argon	10 hr	Run aborted - ZrO_2 electrically isolated from ground.
20b	ZrO_2 (2)	350 W	625°C	Argon	17 hr	ZrO_2 electrically isolated. Poor adhesion to ZrO_2 .
21	ZrO_2 (1) Al_2O_3 (1)	360 W	525°C	25% O_2 75% Argon	16 hr	Black film. Target did not turn green.
22	ZrO_2 (1) Al_2O_3 (1)	200 W	230°C	25% O_2 75% Argon	48 hr	Heated to 600°C prior to deposition. Very good appearing film.
23	ZrO_2 (1) Al_2O_3 (1)	200 W	450°C	25% O_2 75% Argon	31 hr	Poor uniformity.
24	ZrO_2 (1) Al_2O_3 (1)	350 W	350°C	50% O_2 50% Argon	33 hr	Good looking film. Uniformity not as good as Run No. 22.
25	Al_2O_3 (1) ZrO_2 (1) Al_2O_3 electroded	200 W	350°C	25% O_2 75% Argon	56 hr	Similar to Run No. 23.

films were black, as was the starting powder. However, the surface of the target would turn "green" after a series of runs, due to an oxygen deficiency. As noted in Table 1, the addition of oxygen eliminated this problem. In addition, the films have a more uniform appearance. Run No. 21, done at a lower temperature and in 25% oxygen, was very smooth and uniform, with no visible cracks, and was the best appearing film made to date. The same results were obtained for the higher temperature runs, although they were not as good as Run No. 21. This is true, in general, with the very high temperature depositions (625°C) having very poor uniformity. The reason for this is not clear but could be due to a decreased sticking coefficient at elevated temperatures.

5.2.1.2 Fabrication of Interconnection Films by Electrochemical Vapor Deposition (EVD)

A new high temperature reactor and reactor furnace have been assembled. This was necessary for the deposition of modified lanthanum chromite films. Two other existing reactor assemblies allowed deposition temperatures of 1200°C as a maximum. This temperature is not high enough to allow sufficient oxygen ion mobility in the oxide, and the film growth rate that depends on oxygen ion diffusion through the bulk of the film, is slow (1-2 $\mu\text{m}/\text{h}$). It was hoped that a high temperature reactor would alleviate this problem. The new reactor furnace has a 0.6 m long hot zone that reaches 1600°C at the maximum.

The reactor furnace fire-brick insulation had to be totally replaced by the supplier with an alumina felt insulation (the original insulation was not in compliance with pre-purchase quotations and, consequently, the heating rate was excessively slow -- 3h to 1300°C). The new insulation allows a much faster rate of 1 1/2 h to 1350°C, so that a total deposition run of three hours duration can be accomplished during eight working hours.

The total system is in working condition and first deposition runs have been made. These first runs have substantiated the expected increased growth rate of lanthanum chromite films at higher temperatures. In the most recent deposition, a reactor set-up according to Fig. 5 has been used. The outer reactor tube, normally consisting of quartz, has been replaced by mullite in order to resist high temperature and vacuum conditions. Inside reactor linings of graphite have been maintained.

The elevation of the deposition temperature from 1200°C to 1350°C under otherwise similar conditions (vacuum, chloride-delivery) led to a growth rate increase from 1-2 $\mu\text{m}/\text{h}$ to $\sim 10 \mu\text{m}/\text{h}$. A dense, 40 μm thick film was obtained over a 0.15 m long porous zirconia tube, that was covered by a nickel-zirconia fuel electrode. The deposition time was three hours. The arrangement of the substrate tube in the EVD reactor is shown in Fig. 5, indicating how chlorides of chromium

Fig. 5. Reactor Arrangement for EVD of Sr-Doped LaCrO_3 Interconnection Films at Temperatures above 1200°C

lanthanum and strontium are delivered, mixed and flow over the outside of the substrate tube. The substrate tube (porous support tube plus fuel electrode) is mounted in a fixture that is shown in Fig. 6, which depicts how water vapor/hydrogen mixture flows through hose 10 and alumina compression tube 4 to pass between substrate tube 1 and compression tube 4 in order to provide protection of the fuel electrode from oxidation (hydrogen) and oxygen for the film growth (water vapor). A spring 9 provides an elastic means of holding the ceramic assembly firmly together and is located in the cold part of the reactor tube.

5.2.1.2.1 Characterization of Lanthanum Chromite EVD Films

The greatly increased film thickness of the deposit, allowed (for the first time) more rigorous analysis of the material with respect to phase purity and conductivity.

The film deposited by the EVD process from an atmosphere containing lanthanum, chromium, and strontium chlorides was examined by powder X-ray diffraction. The diffraction pattern was similar to that of undoped lanthanum chromite. Elemental analysis of the same film by the direct imaging mass analyzer (DIMA), as compared to a standard sample of $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3$, showed the presence of lanthanum and chromium, but only a trace of strontium, indicating that the conditions of concentration and temperature were not appropriate to provide the desired strontium doping.

Elemental Identification by the Energy Dispersion X-Ray Analyzer (EDAX) confirms an approximately one-to-one ratio of lanthanum and chromium in the film.

Scanning electron microscope (SEM) pictures of a fracture cross section of the film are shown in Fig. 7. These show a coherent, uncracked film with no evidence of porosity. The data suggest that alterations to provide alkaline earth doping remain as the major problem facing the EVD process for making lanthanum chromite interconnections. Fig. 7 shows excellent adherence of the film to the fuel electrode. The

- 1 Substrate Tube
- 2 Alumina Nose Cone
- 3 Alumina Holder Tube
- 4 Alumina Compression Tube
- 5 Alumina Pivot

- 6 Zirconia Powder Packing
- 7 Threaded Brass Sleeve
- 8 Brass Nut
- 9 Steel Spring
- 10 Rubber Hose

Fig. 6. Arrangement of Substrate Tube and Holder for Electrochemical Vapor Deposition of Electrolyte and Interconnection Oxide Films

1

2

3

20 micrometers

A. Fracture cross section of EVD film, nickel electrode, and support tube.

1. Porous zirconia support tube
2. Porous nickel electrode
3. Lanthanum chromite EVD film

5 micrometers

B. Surface of EVD film.

Fig. 7. Lanthanum Chromite EVD Film on a Porous Nickel Electrode

apparent smaller film thickness in the micrograph results from the fracture of the film, that must have broken off, tangentially, a major portion of the film.

5.2.1.2.2 Summary of Work Regarding EVD of Modified Lanthanum Chromite

Very important progress has been made in the fabrication of thick and dense films of lanthanum chromite. The fact that a 40 μm thick deposit on a porous zirconia support tube does not lead to cracking of the latter is significant because a chromium oxide film (the prior state-of-the-art interconnection film) of that thickness would lead to multiple tube fractures. This demonstrates the improved match with respect to thermal expansion of the lanthanum chromite.

The electrical measurements, as reported, as well as the EDAX results indicate, that little or no strontium was incorporated into the lanthanum chromite film. As a result, much refining and modification of chloride delivery and doping remains to be done in the future. It is assumed that this is a relatively minor problem, requiring specific process parameter definition, compared with that of a more basic problem of finding a process capable of deposition of the interconnection material in gas impervious, thin films.

5.2.2 Subtask 2B. Fabrication of the Solid Oxide Electrolyte

The solid oxide electrolyte film component of the fuel cell will be fabricated by the electrochemical vapor deposition technique. This technique, described in detail elsewhere⁽⁸⁾, produced the required 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. In the annual and fifth quarterly report⁽⁹⁾, the new features of the CVD reactor and their successful application were demonstrated by the reproducible results of three successive CVD-experiments: $\text{IN}_{\text{II}}-1$, $\text{IN}_{\text{II}}-2$, $\text{IN}_{\text{II}}-3$. Alumina tubes were used as substrates in these experiments. During this quarter, additional CVD experiments were carried out and included calcia-stabilized zirconia tubes as targets. Both ZIRCOA's (Zirconium Corporation of America)-stabilized tubes and those made in this laboratory were used.

The room temperature profile or film resistance, ρ/δ ($\Omega\text{-cm/cm}$), of the vapor stream exposed length of the target tubes of several of these experiments are shown in Fig. 8. Experiment No. $\text{IN}_{\text{II}}-4$ was the fourth in succession of the above mentioned experiments⁽⁹⁾. A Westinghouse made zirconia target tube was used in this experiment. The ρ/δ vs distance profiles of the other four experiments shown in Fig. 8 constitute two separate duplicate sets (i.e., $\text{IN}_{\text{II}}-5/\text{IN}_{\text{II}}-6$ and $\text{IN}_{\text{II}}-7/\text{IN}_{\text{II}}-8$). The first set of the four experiments and each one of these two was carried out with a new quartz O_2 /steam distributor. In the case of the duplicate set of experiments $\text{IN}_{\text{II}}-5$ and $\text{IN}_{\text{II}}-6$, the holes of this tube were not of the same size. Whether or not this caused the observed small deviation from the plateau of the room temperature ρ/δ - values along the length of the target tubes in these two experiments is not known. The data on Fig. 8, however, show also satisfactory overall reproducibility.

Fig. 8. Resistivity Profile of CVD Tin-Doped Indium Oxide Films on Ceramic Target Tubes.

Δ - Run # IN_{II}-4 [Stabilized ZrO₂ Tube (Westinghouse)].

O - Run # IN_{II}-5 [on Stabilized ZrO₂ Tube (ZIRCOA)].

$\square$ - Run # IN_{II}-6 [on Al₂O₃ Tube].

O - Run # IN_{II}-7 and $\square$ - Run # IN_{II}-8 [on Al₂O₃ Tube].

The ρ/δ values were also measured as a function of temperature (T) for some of the films. These data were obtained in air and at 50° intervals between room temperature and 1000°C. Figs. 9, 10, and 11 give both the heating and cooling ρ/δ vs T curves of films on "Al₂O₃" and "ZrO₂" target tubes. For clarity the data points were omitted and only the curves traced through them are shown here. The specific conditions are identified on each figure. Examination and comparison of all these ρ/δ vs T curves do not allow any conclusions at this time. Several observations, however, can be made. The heating and cooling curves are not reversible. Also, the curves are not reproducible from one thermal cycle to the next. The ρ/δ values increase with increasing temperature and go through a narrow or a broad maximum at $\geq 600^\circ\text{C}$. The maximum close to 600°C is followed by a sharp drop and the overall curve becomes "bell shaped". The maxima above 600°C are broad and are followed by a small decrease or tapering-off up to the highest temperature (1000°C) of these measurements. The ρ/δ values at the temperature of interest (1000°C) are within the desired range for the film thickness range of interest (20-50 μm). There is no correlation between the type of target tube and the ρ/δ vs T behavior of these films. The location of the maxima shifts to lower temperatures as the absolute ρ/δ values increase for each film and thermal cycle. It is interesting to note that the "bell shaped" curve with maximum close to 600°C was only observed during heating and in the two cases where the ρ/δ value in the neighborhood of 600°C was more than twice or a factor of 10 higher than all other cases. The cooling curve a' of Fig. 11 is an anomaly to the general trend of all other cooling curves. Contamination of the original reactants, target tubes and/or the films on handling and prolonged heating may be suspected for the above observed inconsistencies in the ρ/δ vs T behavior. Resistivity ($\Omega\text{-cm}$) measurements on the reactant oxide material were also carried out. For this, a sintered (1500°C in air for 17 hours) square bar specimen of tin-doped indium oxide was used. The dimensions in cm of this bar specimen were: 4.8 x 0.82 x 0.93. The bar had been prepared using conditions identical to those used for the pelletized

Fig. 9. Resistivity Per Unit Thickness (ρ/δ) vs Temperature of Tin-Doped Indium Oxide Film on Alumina Tube (Run # INII-1).

Fig. 10. Resistivity Per Unit Thickness, ρ/δ vs Temperature of Tin-Doped Indium Oxide Film on Zirconia Tubes

Fig. 11. Resistivity Per Unit Thickness, ρ/δ , vs Temperature of Tin-Doped Indium Oxide Film on Calcia Stabilized Zirconia Tubes Supplied by Zirconium Corporation of America (ZIRCOA)

reactant oxide samples. Two heating and one cooling $\rho(\Omega\cdot\text{cm})$ vs T curves were obtained. The behavior was similar to that shown in Fig. 9 and it is not shown here. This result tentatively suggests stricter control of the impurities of the materials that may be needed. More detailed work will be needed to study the effect of various impurities on the ρ /vs T behavior of this system. The present emphasis is not centered on this aspect of the problem.

The $\rho(\Omega\cdot\text{cm})$ values of the bar specimen range from 1.5×10^{-3} to $\sim 8.0 \times 10^{-3}$ between room temperature and 1000°C . This order of magnitude provides indirect proof of solid solution formation between SnO_2 and In_2O_3 under the conditions that the reactant oxide pellets are prepared. Independent evidence of solid solution formation comes from microscopic examination of the pellets and their complete solubility in a HCl/HNO_3 solution where it is known that free SnO_2 is not soluble.

The average ρ/δ values of some of the films at room temperature and 1000°C have been used to obtain their $\rho(\Omega\cdot\text{cm})$ values. These values together with those for the film thickness δ (μm) are given in Table 2. The calculated δ in this table was obtained from the film weight, density (7.17 gm/cm^3) and area on the target. This calculation assumes uniform deposits along the entire coated length of the target tube. The results of Fig. 8 and those of the previous report⁽⁹⁾ justify this calculation here. The measured δ values were obtained from micrographs of the size shown in Fig. 12. These micrographs are typical of many taken along the length of the target tubes of Run Nos. $\text{IN}_{\text{II}}-1$ and $\text{IN}_{\text{II}}-4$. They demonstrate the impervious nature of the deposited films and the smoother surface of the alumina tubes (Fig. 12a) than that of the zirconia tubes (Fig. 12b) that are currently made by Westinghouse. For each micrograph of the size shown here, 24 equidistant δ measurements were taken and the average value of each location that was photographed was recorded. The figures in the table, i.e., $47.0 \mu\text{m}$ and $38.6 \mu\text{m}$, are the average of 3 and 8 locations along the target tubes of runs $\text{IN}_{\text{II}}-1$ and $\text{IN}_{\text{II}}-4$, respectively. The agreement between the calculated and measured δ values is

TABLE 2

Film Thickness, Resistivity and Chemical
Analysis Data of As-Prepared Films

Run No.	Film Thickness, δ , (μm)		Resistivity, ρ , ($\Omega\cdot\text{cm}$) at		Chemical Analysis (wt %)*	
	Calc'd.	Meas.	Room Temp.	1000°C	Sn	In
IN _{II} -1	44.2	47.0	2.0×10^{-4}	5.5×10^{-4}	1.8	78.7
IN _{II} -2	43.3	--	2.0×10^{-4}	--	1.9	80.2
IN _{II} -3	42.9	--	2.0×10^{-4}	--	1.9	79.6
IN _{II} -4	39.1	38.6	2.0×10^{-4}	6.1×10^{-4}	1.7**	70.8**

*The Atomic Absorption spectrophotometric method was used.

**The solution of this sample contained some Ca and Mg due to the solubility of the free (non-stabilized) portion of CaO and MgO of the zirconia target tube. When this is taken into account, the estimated wt % values of Sn and In of the film will be close to 1.9 and 80.0, respectively.

(a)

(b)

Fig. 12. Micrographs Showing the Type of Films Obtained from CVD Experiments $IN_{II}-1$ (a) and $IN_{II}-4$ (b)

[Average film thickness: (a) $43.1 \mu m$; (b) $38.1 \mu m$].

excellent and it shows that once a uniform room temperature ρ/δ vs distance profile is obtained, the time consuming metallographic approach is not necessary for measuring the thickness of the tin-doped indium oxide films. The data of chemical analysis of the films of the first four successive experiments are also listed in Table 2. The wt % values for Sn and In show, within the analytical accuracy, film composition uniformity upon continuous exposure of the reactant oxide pellets to the incoming reactive NH_3/HCl gas mixture. The duration of each one of these experiments was 60 minutes. Three reactant oxide pellets were also analyzed and after the total exposure of the four runs listed in Table 2 (i.e., 240 minutes). The average wt % values of Sn and In of these pellets before exposure were: 1.70 and 82.4, respectively. The corresponding average wt % values after the 240 minute exposure were: 1.67 and 80.0. These results again show the absence of distinguishable preferential reactivity of the two oxide components of the reactant oxide material and demonstrate that the sample preparation procedure used and the chosen CVD-conditions are satisfactory

The previously reported⁽¹⁰⁾ thermal expansion measurements of a pressed and sintered bar specimen of tin-doped indium oxide were repeated with the addition of 2 wt % Kaolin to the powder mixture of SnO_2 and In_2O_3 that was used for its preparation. These new measurements show slightly increased thermal expansion values throughout the entire temperature range (room temperature - 1000°C). The new coefficient of expansion α at 1000°C is $9.23 \times 10^{-6} \text{ m/m/}^\circ\text{C}$. The previous value was $8.95 \times 10^{-6} \text{ m/m/}^\circ\text{C}$ ⁽⁹⁾. If Kaolin does not enter the lattice of tin-doped indium oxide and serves only as a sintering agent, then this latest value can be considered an improvement over the previous value since it is closer to the value of $9.5 \times 10^{-6} \text{ m/m/}^\circ\text{C}$ reported in the literature,⁽¹¹⁾ and closer to the value of the yttria-stabilized zirconia electrolyte.

5.2.3.1 Summary

Air electrode current collector tin-doped indium oxide films are being produced by chemical vapor deposition (CVD), with uniform

thickness over about 10 inches of tube length. Characterization of these films shows that they have uniform composition upon continuous use of the starting reactant oxide material in the CVD process. Desired film thickness (20-50 μm) and resistivity values ($\approx 10^{-3} \Omega\text{-cm}$) are being achieved.

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⁽¹²⁾.

A typical electrode has a resistance of 0.05 Ω/square at room temperature. The resistance increases to nearly 0.3 Ω/square at 1000°C. The electrode resistance of presently fabricated electrodes is considered to be too high, by a factor of three. However, the resistance can be lowered by three methods: a) by increasing surface loading, b) by increasing nickel content in the cermet, c) by electroplating nickel onto the existing cermet structure. All three methods will be investigated, if necessary, to enhance the fuel electrode conductivity.

Fuel electrode fabrication, as described in the Fifth Quarter report of July 18, 1977,⁽¹²⁾ leads to well performing electrodes. The conductivity of these electrodes, however, needs improvement. This can only be done by increasing the nickel content in the electrode. If this is accomplished by sintering, one finds that it leads to a weaker mechanical structure because of a reduced zirconia content, which stabilizes the electrode structure.

Electroplating has been considered as a possible method of increasing the nickel content of the electrode and maintaining the strong sintered zirconia skeleton in the electrode. An experimental set-up as shown in Fig. 13 has been used for plating. The nickel anode was placed inside the porous tube in order to plate the nickel throughout the nickel-cermet electrode and not simply on top of the electrode (which would reduce adherence to electrolyte and possibly cause a dense polarizing nickel film).

- 1 Porous Tube
- 2 Ni-ZrO₂ - Cermet Fuel Electrode
- 3 Ni-Contact Wire
- 4 Ni-Anode
- 5 Rubber Stopper
- 6 Glass Container
- 7 Ni-Sulfamate Plating Solution

Fig. 13. Arrangement for Nickel Plating of Fuel Electrodes

Fig. 14 shows the resistance decrease of an electrode if the nickel content of 7 mg/cm^2 is increased to 23 mg/cm^2 . It is assumed that the more than a factor of three improvement in conductance is a result of connecting electrically insulated nickel islands in the sintered cermet structure and thickening of small contact areas between nickel particles.

In total, it can be said that nickel electroplating is an effective means of reducing fuel electrode resistance to an acceptable level. It is assumed that this will not impede electrode performance, however, this fact must be established in cell tests.

Future plans in fuel electrode improvement include more electroplating experiments and, also, a new electrode application technique by transfer-tapes will be investigated in order that present fuel electrode etching and cleaning procedures might be eliminated.

5.2.5 Task 2D. Porous Support Tube Fabrication

Fabrication of porous tubes from loose particulate matter, (such as powders of calcia-stabilized zirconia $[(\text{ZrO}_2)_{0.85}(\text{CaO})_{0.15}]$ having a thin wall of $\sim 1000 \mu\text{m}$) starts with a forming process(13-16) that leads to green bodies of high strength with controlled porosity in the fired state and a uniform surface texture down to a microscopic scale. Texture is emphasized because particle orientation plays an essential role in the densification of a porous ceramic structure.

Tubes formed from p/s ratio* of 2.33 with starting powders of 70 w/o (-325 mesh +400): 30 w/o (-400 mesh +500) and 70 w/o (-400 mesh +500): 30 w/o (-500 mesh) demonstrated that selected grain size distribution blends achieved high porosity ($\sim 30\%$) without burn out additives.

*p/s = primary/secondary powder material.

Fig. 14. Fuel Electrode Resistance Changes With Temperature and Reduction of Resistance by Electroplating

The combination of higher temperature calcined material ($\sim 1780^{\circ}\text{C}$) and blending the powder into p/s fractions produced good quality substrate with the desired porosity range specified for the fuel cell support tube.

Material supplied by Zircoa was given first priority for evaluation during this quarter. Zircoa material produced good quality, inhouse porous tubes that, in general, compare favorably with the physical properties of the tubes fabricated Zircoa from the same lot of material. Zircoa formed their porous tubes by slip casting, using 70 w/o or particles in the 44-10 μm range and 30 w/o of particles under 10 μm .

Forming and densification of porous support tubes from several material lots produced in the laboratory are in progress at the various stages of process at this time.

5.2.5.1 Powder Preparation

Starting powders of calcia-stabilized zirconia $[(\text{ZrO}_2)_{0.85}(\text{CaO})_{0.15}]$, required for the extrusion of high porosity thin wall tubing, were formulated and prepared in house and also obtained from a commercial supplier to our specifications. Batches (2000 grams) of formulated material were mixed in a ball mill, dried, and pressed into cylindrical "slugs" and calcined at 1780°C for one hour. A rotary steel disk crusher was utilized to reduce the calcined material to less than 100 mesh, prior to ball milling to minus 325 mesh. A magnetic separator (Ferro-Franz Filter) was used to remove any iron particles in the milled slurry that may have been picked up during the crushing operation. The dried powder was classified by screening into the following particle sizes; -325 +400, -400 +500 and -500 mesh.

5.2.5.2 Paste Preparation

Ceramic pastes were prepared, starting with a mixture of powder fractions and blending them with plasticizers, water and wetting agent. A kneading machine (Baker-Perkins) was used to homogenize the

material (500 gram batch) to the right plasticity for extrusion. To facilitate handling and processing each batch was designed to yield 5 feet of extruded tubing.

Powder fractions prepared for extrusion were 70 w/o (-325 +400): 30 w/o (-400 +500) and 70 w/o (-400 +500): 30 w/o (-500 mesh) material with a primary/secondary powder ratio of 2.33.

Data for this report are based on 8 w/o calcia-stabilized zirconia powder made to Westinghouse specifications by Zircoa.*

Fig. 15 shows the particle size analysis of the sieve fractions of the material lot supplied by Zircoa. Fig. 16 is the particle size analysis of the starting material, identified as batches A and B.

5.2.5.3 Forming and Densification

Tubes were extruded using the die setup as reported earlier⁽¹⁷⁾ from the plastic ceramic paste and transferred to grooved trays for drying in a humidity drying oven. Drying conditions (of 110°C dry bulb temperature with a wet bulb temperature of 80°C) were maintained for 4 hours. After the tubes were dried the initial presintering (~2400°F) was accomplished by "hang fire" in a vertical position or bedded down horizontally on refractory zirconia sand. The firing conditions were selected according to the length of the tubing to match furnace capacity. Presintering firing schedules were adopted to minimize problems of binder burn out and to assure dimensional stability of the tubing for the high temperature firing at 1800°C. Short samples for evaluation of batching parameters were fired in a Centorr furnace and tubes 5-6 inches, as required for experimental fabrication of fuel cells, were fired in a gas furnace. The final sintering temperature was 1800°C with variation in firing time.

*Zircoa - Division of Corhart Refractories Company, Corning Glass Works.

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Fig. 15. M. S. A. Sedimentation Particle Size Analysis of Zircoa 8 w/o Calcia-Stabilized Zirconia

Fig. 16. M. S. A. Sedimentation Particle Size Analysis of Zircoa 8 w/o
Calcia-Stabilized Zirconia

5.2.5.4 Results and Discussion

The use of the Baker-Perkins kneading machine improved the workability of the batch mix of loose particulate powder for fraction and plasticizer to a plastic mass that can be easily and conveniently extruded into thin wall tubes of sufficient green strength.

Powder fraction with p/s ratio of 2.33, using two different particle size fraction combinations, produced tubes above 30% porosity. Table 3 shows the properties of tubes made by extruding 15 m/o calcia-stabilized zirconia powder from Zircoa. Firing the tubing at 1800°C for 2 hours decreased the porosity by approximately 4% (decreased from 35 to 31%).

Table 4 shows comparison of data on the same lot of tubes made by slip casting from Zircoa. Westinghouse data shows low apparent porosity as compared to Zircoa's data (35% vs 28%).

Figs. 17 and 18 show photographs of the interior and exterior of the slip cast tubes from Zircoa. The pores appear uniform and in the order of 5-10 μm in size.

5.2.5.5 Summary

Forming and densification of particle size fraction with p/s (primary/secondary), ratio of 2.33 by extrusion and firing to 1800°C produced tubes with porosity in the 31-34 percent range.

Work is continuing to optimize the p/s ratio of the particle size fractions, using in-house starting materials.

Negotiations with a second commercial supplier have been initiated for a limited quantity of materials and 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.

TABLE 3

Data of Tubing Made by Extrusion, Using
Powder Supplied by Zircoa

Batch A

	Bulk Density (g/cc)	Percent Apparent Porosity	Apparent Specific Gravity (g/cc)
70 w/o -325 +400			
30 w/o -400 +500			
1800°C 1 hr	3.07	35.06	4.72
1800°C 2 hr	3.29	31.14	4.78

Batch B

70 w/o -400 +500			
30 w/o -500			
1800°C 1 hr	3.09	36.48	4.86
1800°C 2 hr	3.39	31.10	4.93

TABLE 4

Data of Tubing Supplied by Zircoa

	Bulk Density (g/cc)	Percent Apparent Porosity	Apparent Specific Gravity (g/cc)
Zircoa	3.56	36.1	
	3.56	35.0	no data
	3.62	34.0	
(W) Data	3.64	28.0	5.10
	3.74	28.60	5.16

180X
55 $\mu\text{m}/\text{cm}$

450X
22 $\mu\text{m}/\text{cm}$

Fig. 17. Exterior Surface of 8 w/o Calcia-Stabilized Zirconia Tubes from Zircoa

180X
55 $\mu\text{m}/\text{cm}$

450X
22 $\mu\text{m}/\text{cm}$

Fig. 18. Interior Surface of 8 w/o Calcia-Stabilized Zirconia Tubes from Zircoa

5.3.1 Subtask 3A. Interconnection Testing

In the Fifth Quarter report⁽¹⁸⁾, we discussed the measurement of interconnection material resistivity by means of thin film specimens deposited on alumina substrates. These measurements were made with the current flow parallel to the substrate which minimized any contact resistance problems. Our results showed that $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ should be an excellent interconnection material since it exhibited a high, stable conductivity both in air and in hydrogen-water atmospheres. Although more specimens of this type have been prepared, measurements on them have been deferred in order to accelerate the preparation and measurement of combination specimens, discussed in the next section.

5.3.2 Subtask 3B. Combination Testing

Combination testing of interconnection material involves an additional fuel cell component (fuel electrode or air electrode) and is carried out with the current flow perpendicular to the plane of the interconnection film, just as it will occur in an operating fuel cell. For good interconnection materials, the resistance measured will be quite low (milliohms) and contact resistance at the component interface may become important. Suitable measurement techniques, discussed in the Fifth Quarter report, p. 48ff, are provided by the two- or three-contact method and the crossed-electrode method.

5.3.2.1 Two Contact Measurement on a $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ Specimen

Measurements of the two-contact type were carried out on a tubular specimen similar to that shown in Fig. 19. It consisted of a porous stabilized-zirconia substrate tube plus a nickel-zirconia cermet fuel electrode on which a 40-50 micron thick layer of $\text{La}_{1-x}\text{Sr}_2\text{CrO}_3$ (strontium-doped lanthanum chromite) had been deposited by the EVD process. It was planned to deposit pure nickel electrodes on the surface for the measurements, however, the R.F. sputtering facility was unavailable at that time. Instead, platinum paste electrodes were applied, using four repetitions of masking, paste application, and firing

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Fig. 19. Tubular Combination Specimen With Contacts for Two- or Three-Electrode Resistance Measurements

at 1000°C in hydrogen-water to avoid oxidation of the fuel electrode layer. Resistance measurements were carried out in hydrogen-water at temperatures between 400°C and 1000°C. The effective resistivity of the interconnection layer was calculated from the measurements and appears in the graph of Fig. 20.

The most striking aspect of the data is the extremely high resistivity, 20,000 ohm-cm at 1000°C, with some hysteresis toward higher resistivity values. We do not believe an interface resistance between the fuel electrode and interconnection material can account for this very high value. If this were the case, there would still be a measurable lateral resistance between adjacent Pt surface electrodes at room temperature; our measurements indicated $R > 10^9$ ohms, beyond the limit of our apparatus. The most likely explanation, discussed in an earlier section, is that the material was essentially undoped lanthanum chromite for which one would predict a high resistivity, especially when measured in a reducing atmosphere. The hysteresis effect is apparently due to the gradual equilibration of the specimen with the reducing atmosphere.

5.3.2.2 Preparation of Crossed-Electrode Specimens

In order to test the effectiveness of the crossed-electrode technique (discussed in the Fifth Quarter report)⁽²⁰⁾ for measurement of very low combination specimen resistances, a special test specimen, shown in Fig. 21, is being prepared. It consists of an alumina substrate, a platinum base electrode (5 microns thick), a film of interconnection material ($\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$, 18 microns thick), and two platinum top electrodes (5 microns thick) at right angles to the base electrode. The first two depositions have been completed, with the final deposition awaiting availability of the platinum sputtering facility. This specimen should enable us to judge the value of the crossed-electrode technique for low resistance combination specimen testing.

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Fig. 20. Resistivity Vs. Temperature for a Tubular Combination Specimen (45 Micron Layer of $La_{1-x}Sr_xCrO_3$ Deposited by EVD on Ni-ZrO₂ Cermet Fuel Electrode. Measurement in Hydrogen-Water Atmosphere)

Fig. 21. Test Specimen for Evaluation of Crossed-Electrode Technique for Measuring Low Resistance Interconnection Films

5.4 TASK 4. ALTERNATE ELECTROLYTE AND BATTERY DESIGNS

Work in this area consists of:

- a. 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,
- b. modifying 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 (a), 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 (members with Westinghouse on the ERDA, 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 (b), will be evaluated, only if problems to the present Westinghouse design, using the best component materials that have been identified, are detected.

5.5 VAPOR TRANSPORT STUDIES ON INDIUM OXIDE AND INTERCONNECTION MATERIAL

Long term exposure of oxides to water vapor containing gases, as air and fuel or oxidized fuel, can lead to material losses by vapor transport. While vapor pressures of oxides might be low and indicate long component life, vapor transport reactions can, possibly, deleteriously affect actual operational life. The transport can happen through the formation of suboxides, hydroxides or oxihydroxides, due to the presence of water, particularly at low oxygen partial pressures. Valence changes or equilibrium conditions and temperature gradients favor these transport reactions.

Indium oxide is subjected to such an environment (high oxygen partial pressure, moist air); also the interconnection material (moist air on one, moist fuel on the other side) could suffer from vapor transport.

We have started experimentation, using a microbalance system to measure losses by vapor transport on both of these substances. Data today are inconclusive, due to problems of measuring small weight changes in flowing gases at atmospheric pressure. We are investigating other techniques to measure vapor transport of indium oxide and interconnection .

6.0 SUMMARY OF FUTURE PLANS

According to the outline of the design plan⁽²¹⁾ the following work plans are projected for the seventh 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

Oxygen loss from $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_{3-x}$ as a function of oxygen pressure will be measured in a manner similar to that made for the $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_{3-x}$ composition, to help ascertain if oxygen leakage through an interconnection film of this material is likely to be low.

The EVD process variables will be altered to incorporate an alkaline earth constituent in the films.

RF sputtered films of $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ will be made on nickel electrode substrates at temperatures near 500°C to provide an anode electrode-interconnection interface which does not crack during the post-sputtering heat treatment.

Subtask C. Development of Other Stack Components

Work here will actually be concentrated on the fabrication techniques and evaluation of the thin films produced by these techniques, since the air, fuel, electrolyte and support tube materials have essentially been identified.

Task 2. Fabrication Techniques

Subtask A. Interconnection

Work will continue on the EVD process for preparation of the lanthanum chromite film. Refining and modification of the process, particularly, to enhance strontium delivery, will occur.

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

CVD experiments of tin-doped indium oxide films will continue with zirconia target tubes of modified surface roughness in order to aim at producing the desired porous electrode film collector material. CVD experiments will be made on interconnection films and on EVD-deposited solid electrolyte films in order to gain experience necessary for the ultimate fabrication of a fuel cell stack.

Electroplating of additional nickel to the fuel electrode structure will continue. Also, a new electrode application technique, by transfer tapes, will be investigated in order that present fuel electrode etching and cleaning procedures might be eliminated.

Subtask D. Porous Support Tube

Work will continue to optimize the p/s ratio of the powder particle size fractions, using in-house starting materials.

Delivery of porous support tubes, fabricated in-house, to meet needs of other tasks of the program, will continue.

Exploration of another commercial vendor source of porous support tubes will continue.

Task 3. Component Testing

Subtask A. Interconnection

Resistivity measurements on thin film specimens (tangential current flow) will be continued.

Subtask B. Combinations

Measurements will be continued on tubular combination specimens with EVD-deposited interconnection films. The crossed-electrode specimen will be tested and the technique evaluated for application to combination test specimens and complete cells.

Subtask C. Useful Life Testing

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

Task 4. Alternate Electrolytes and Battery Designs

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

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

7.0 REFERENCES

1. C. J. Warde, R. J. Ruka, and A. O. Isenberg, "Energy Conversion Alternatives Study (ECAS), Westinghouse Phase I Final Report, Vol. XI, Fuel Cell", Contract No. NAS-3-19407, NASA Lewis Research Center, February 12, 1976, p. 13-88.
2. J. Weissbart and R. Ruka, Rev. of Sci. Inst., 32, 593 (1961).
3. J. Weissbart and R. Ruka, J. Electrochem. Soc., 109, 723 (1962).
4. H. Anderson, Reported at Workshop on High Temperature Solid Oxide Fuel Cells, held at Brookhaven National Laboratory, May 5 and 6, 1977.
5. B. Rossing, private communication.
6. Thin Film Fuel Cell/Battery Power Generating System, Fifth Quarter Report, ERDA Contract EY-76-C-03-1197, Westinghouse Electric Corporation, July 18, 1977, pp. 18-20.
7. Ibid., p. 12.
8. Thin Film Battery/Fuel Cell Power Generating System, First Annual Report (for the period April 1976 - April 1977), ERDA Contract EY-76-C-03-1197, Westinghouse Electric Corp., April 30, 1977, pp. 37-40.
9. 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. 22-32.
10. Thin Film Battery/Fuel Cell Power Generating System, First Annual Report (for the period April 1976 - April 1977) ERDA Contract EY-76-C-03-1197, Westinghouse Electric Corporation, April 30, 1977, pp. 50-63.

REFERENCES (Continued)

11. K. D. Kundra and S. Z. Ali, J. Appl. Cryst. (1970) 3, p. 543.
12. Thin Film Fuel Cell/Battery Power Generating System, Fifth Quarter Report, ERDA Contract EY-76-C-03-1197, Westinghouse Electric Corporation, July 18, 1977, p. 33.
13. J. Williams, "Characteristics and Preparation of Ceramic Powders," Processings of the British Ceramic Society, No. 3, Oct. 1965, Fabrication Science, p. 1.
14. A. W. Hey and D. T. Livey, "Calcination Process in Oxide," Proceedings of the British Ceramic Society, No. 12, March 1969, Fabrication Science 2, published by the Society Stoke-on-Trent, p. 13.
15. A. L. Stuijts and G. J. Oudemans, "Ceramic Forming Methods," Proceedings of the British Ceramic Society, No. 3, Oct. 1965, Fabrication Science, p. 81.
16. G. Capriz and A. Laratta, "Extrusion of Non-Newtonian Bodies," Proceedings of the British Ceramic Society, No. 3, Oct. 1965, Fabrication Science, p. 123.
17. Thin Film Battery/Fuel Cell Power Generating System, First Annual Report (for the period April 1976 - April 1977), ERDA Contract EY-76-C-03-1197, Westinghouse Electric Corp., April 30, 1977, pp. 65, 66.
18. 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. 48-52.
19. 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. 53-56.
20. 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.

REFERENCES (Continued)

21. Thin Film Battery/Fuel Cell Power Generating System, Task E1, Design Plan, ERDA Contract EY-76-C-03-1197 (Formerly E(04-3)-1197), Westinghouse Electric Corp., June 7, 1976.

8.0 PERMANENT RECORD BOOK ENTRIES

Figuring books, containing information described in this report are:

207720	pp. 114-149
208043	pp. 47, 48, 57-63
207905	pp. 26-38, 40, 41, 44, 46-61, 64-68, 71-81, 83-85
207840	pp. 61-77
207516	pp. 1-7
207096	pp. 44-56
207599	pp. 96-100
208023	pp. 13-24