A SIMULATION MODEL FOR WIND ENERGY STORAGE SYSTEMS

MASTER

Volume I: Technical Report

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16. Abstract <p>The effort developed a comprehensive computer program for the modeling of wind energy/storage systems utilizing any combination of five types of storage (pumped hydro, battery, thermal, flywheel and pneumatic). An acronym for the program is SIMWEST (Simulation Model for Wind Energy Storage). The level of detail of SIMWEST is consistent with a role of evaluating the economic feasibility as well as the general performance of wind energy systems.</p> <p>The software package consists of two basic programs and a library of system, environmental, and load components. The first program is a precompiler which generates computer models (in Fortran) of complex wind source/storage/application systems, from user specifications using the respective library components. The second program provides the techno-economic system analysis with the respective I/O, the integration of system dynamics, and the iteration for conveyance of variables. This SIMWEST program, as described, runs on the UNIVAC 1100 series computers.</p> <p>This technical report contains three volumes. Volume I gives a brief overview of the SIMWEST program and describes the two NASA defined simulation studies. Volume II, the SIMWEST operations manual, describes the usage of the SIMWEST program, the design of the library components, and a number of simple example simulations intended to familiarize the user with the program's operation. Volume II also contains a listing of each SIMWEST library subroutine. Volume III, the SIMWEST program description contains program descriptions, flow charts and program listings for the SIMWEST Model Generation Program, the Simulation program, the File Maintenance program and the Printer Plotter program. Volume III generally would not be required by SIMWEST user.</p>					
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CONTENTS

	<u>Page</u>
1.0 INTRODUCTION	1
1.1 SIMWEST OVERVIEW	2
1.2 SIMWEST LIBRARY	4
1.2.1 Storage Subsystems	6
1.2.2 Logic Components	12
1.2.3 SIMWEST Output	15
1.3 TESTING	15
1.4 OBSERVATIONS	17
1.5 FUTURE APPLICATION	18
2.0 TEST CASE	21
2.1 SYSTEMS OVERVIEW	21
2.2 TEST CASE SPECIFICATION	25
2.3 SUMMARY OF RESULTS	28
2.3.1 Wind Power	28
2.3.2 Storage Subsystems	34
2.3.3 Load Service	43
3.0 PARAMETRIC STUDY	49
3.1 STUDY OVERVIEW	49
3.2 BATTERY SUBSYSTEM	52
3.3 THE THERMAL SUBSYSTEM	54
3.4 PARAMETRIC STUDY SPECIFICATION	57
3.5 SUMMARY OF RESULTS	57
3.5.1 Effect of Load on Cost of Operation	65
3.5.2 Effect of Load Size on Frequency of Operation	69
3.5.3 Effect of Cut in Speed on Frequency of Operation	74
3.5.4 Effect of Initial State of Storage on Frequency of Operation	74
3.5.5 Effect of Storage Capacity on Frequency and Cost of Operation	76
3.5.6 Study of Inverter Efficiency	81

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CONTENTS

	<u>Page</u>
3.6 SUMMARY OF CRITICAL SYSTEM PARAMETERS	84
3.6.1 Wind Turbine-Gear-Generator	84
3.6.2 Rectifier-Battery-Inverter	84
3.6.3 Thermal Vessel	85
3.6.4 Loads	85
4.0 LIST OF REFERENCES	91

LIST OF FIGURES

	<u>Page</u>
1.1-1 SIMWEST Program Organization	3
1.2-1 Pneumatic Storage Subsystem	7
1.2-2 Pumped Hydro Storage Subsystem	8
1.2-3 Flywheel Storage	9
1.2-4 Battery Storage	9
1.2-5 Thermal Storage	10
1.2-6 Example of Power Divider and Accumulator Use	14
2.1-1 SIMWEST Test Case	22
2.1-2 Random Wind Component Density Function	23
2.1-3 Wind Daily Profile	24
2.1-4 Weekly Domestic Load Profile	24
2.2-1 Model Generation Input Data	27
2.2-2 Line Printer Schematics (Page 0 only)	29
2.2-3 Test Case Data Cards (Part 1)	30
2.2-4 Test Case Data Cards (Part 2)	31
2.2-5 Test Case Data Cards (Part 3)	32
2.3-1 Wind Speed Histogram (MPH)	33
2.3-2 Wind Power Histogram (KW)	35
2.3-3 Generator Power (KW) Vs Wind Speed (MPH)	36
2.3-4 Storage State (KWH) Vs Time for Five Storage Subsystems	37
2.3-5 Temperature of Heat Exchanger Outlet	38
2.3-6 Burner Fuel Consumption Rate (LB/HR)	39
2.3-7 Temperature ($^{\circ}$ F) of Pneumatic Storage	40
2.3-8 Power Into Flywheel (KW) Vs Power Generated By Wind	41

FIGURES

	<u>Page</u>
2.3-9 Power Into Flywheel (KW) Vs Battery State of Charge (KWH)	42
2.3-10 Percentage of Domestic Load Met By Battery	46
2.3-11 Percentage of Domestic Load Met By Flywheel	47
3.1-1 Plumbrook Configuration For Parametric Study	50
3.2-1 Battery Cell Voltage Characteristics	53
3.2-2 Battery Model	52
3.2-3 Rectifier and Inverter Efficiencies	55
3.3-1 Temperature Enthalpy Curve For Thermal Vessel Heat Storage Media	56
3.4-1 Model Generation Input Data	58
3.4-2 Schematic Printout (Page 0)	60
3.4-3 Schematic Printout (Page 1)	61
3.4-4 Schematic Printout (Page 2)	62
3.4-5 Parametric Study Input Data	63
3.5-1 Average Wind Turbine Output Power (KW)	64
3.5-2 Monthly Cost of Wind Generated Energy	66
3.5-3 Monthly Energy Cost To Satisfy The Load	67
3.5-4 Monthly Cost of Energy (without storage)	68
3.5-5 Energy Cost With No Purchase From Utility and No Credit For Surplus Power	70
3.5-6 Energy Cost With No Purchase From Utility, No Credit For Surplus and No Storage	71
3.5-7 Effect of Load Size on Frequency of Operation (With Storage)	72
3.5-8 Effect of Load Size on Frequency of Operation (Without Storage)	73
3.5-9 Frequency of Operation For Different Turbine Cut-In Speeds	75
3.5-10 Effect of Storage Size on Frequency of Operation	77
3.5-11 Daily Load Profiles	78
3.5-12 Effect of Storage Size on Cost of Energy to Load	79

FIGURES

	<u>Page</u>
3.5-13 Effect of Storage Size on Cost of Energy to Load (No Utility Available)	80
3.5-14 Comparison of Frequency of Operation For Two Inverter Systems	82
3.5-15 Comparison of Inverter Efficiencies	83
3.6-1 Turbine Power Coefficient Vs Wind Speed	86
3.6-2 Gear Loss (KW) Vs Input Power (KW)	87
3.6-3 Curve Used For Rectifier Efficiency	88
3.6-4 Curve Used For Inverter Efficiency	89

LIST OF TABLES

	<u>Page</u>
1.2-1 SIMWEST Library Components	5
1.2-2 Partial List of Component Inputs and Outputs	11
2.1-1 Characteristics of Storage Subsystems	26
2.3-1 Load Service Breakdown	45
2.3-2 Storage Subsystem Efficiency	48

FOREWORD

This report presents results of work conducted by Boeing Computer Services Company under NASA Contract NAS3-20385, "Wind Energy Storage Model Development." This program was conducted under the sponsorship of the Advanced Physical Methods Branch, Office of Conservation, ERDA, under the direction of Dr. G. C. Chang, and was administered by the NASA-Lewis Research Center Thermal and Mechanical Storage Section with Mr. L. R. Gordon as Project Manager. This report is in three volumes.

- I. Technical Report
- II. Operation Manual
- III. Program Descriptions

The Boeing Program Manager for this work was R. W. Edsinger, and A. W. Warren was the principal investigator.

For completeness, the summary sections 1.1 and 1.2 of Volume I have been repeated in the Operation Manual, Volume II.

1.0 INTRODUCTION

The need for energy storage for solar energy systems (wind, thermal, heating and cooling, and photovoltaic) is generally recognized. However, until recently a comprehensive computer model for evaluating the type and quantity of storage for a given application did not exist. In November of 1976 NASA-Lewis, as project manager for ERDA, awarded a contract to Boeing Computer Services (BCS), to develop such a model. It is called SIMWEST (Simulation Model for Wind Energy Storage). SIMWEST was required to have the capability of modeling wind energy/storage systems utilizing any combination of five types of storage (pumped hydro, battery, thermal, flywheel and pneumatic). The level of detail of SIMWEST was to be consistent with a role of evaluating the economic feasibility and general performance of wind energy systems. The SIMWEST design was to facilitate its adaptation to other solar applications and other levels of detail.

To meet these requirements BCS developed the SIMWEST based upon an existing dynamic simulation model (EASY). It consists of a library of system components and a precompiler program which allows these components to be put together in building block form. The SIMWEST program, as described here runs on the UNIVAC 1100 series of computers.

Other computer programs exist for the simulation of wind systems and various forms of energy storage. However, SIMWEST is the only publicly available program capable of simulating total wind systems containing any one or combination of the above types of storage and at the same time having the flexibility and depth required to perform thorough and meaningful parametric studies.

Volume I of this report gives a brief overview of the SIMWEST program and describes the two, NASA defined simulation studies including a definition of the systems simulated, the data cards used and a summary of the simulation results. Volume II, the SIMWEST operations manual, describes the usage of the SIMWEST program, the design of the library components, and a number of simple example simulations intended to familiarize the user with the program's operation. Volume II also contains a listing of each SIMWEST library subroutine. Volume III, the SIMWEST program description contains program descriptions, flow charts, and program listings for the SIMWEST Model Generation Program, the Simulation program, the File Maintenance program and the Printer Plotter program. Volume III generally would not be required by a SIMWEST user.

1.1. SIMWEST OVERVIEW

SIMWEST consists of two basic programs, and a library of system, environmental, and load components. The first program, the Model Generation Program, is a precompiler which generates computer models (in FORTRAN) of complex wind energy generator/storage/application systems, from user specifications using SIMWEST library components. The second program exercises the resulting computer model to perform cost and potential utilization analysis. It handles input, output, integration of system dynamics, and iterates to obtain convergence of variables involved in implicit loops. The combination of these two programs provides a powerful tool for analyzing alternate storage system designs.

Figure 1.1-1 shows the general organization of the SIMWEST program. In addition to the two programs described above, there is a third which performs file maintenance. It is used to incorporate user supplied data for new subsystem models. Although the program is shown to be made up of a number of subprograms, it can be executed as a single batch program by supplying the model description control cards and the control cards describing the desired analysis to be performed and the desired tabular and/or plotted output.

FIGURE 1.1-1 SIMWEST PROGRAM ORGANIZATION

1.2 SIMWEST LIBRARY

The SIMWEST library is listed in Table 1.2-1. It is made up of five types of components: physical, environmental, load, logical, and utility.

Physical components encompass such things as motors, generators, transmissions, flywheels, etc. These components model actual physical hardware which might be used in a wind energy system. The selection of the particular SIMWEST library set of physical components was based on the requirement that it be capable of modeling the five types of energy storage systems mentioned previously: thermal, flywheel, battery, pumped hydro and pneumatic.

The degree of detail in the component models is based upon two design criteria. First, all models should contain sufficient detail to simulate all physical characteristics and constraints having significant impact on the systems overall cost effectiveness. Second, the models should be designed to minimize computer time and required user specification. It is assumed that a typical SIMWEST simulation might cover a time span of one year. Thus, from a computer run time and economic impact point of view a simulation step size of between 15 minutes and one hour seemed reasonable.

As a result of the above two design criteria, many physical components, such as the electrical components, were modeled mainly in terms of power flow and steady state response. This lack of detail is consistent with the 15 minute time step and with the concept that the important transients are on the time scale of demand curves or weather patterns, i.e., an hour or more, rather than on the time scale of electric motor transients of a few seconds. If short electric transients were to be modeled, much detail would need to be added to the component models which would greatly increase the user's task of specifying the model. Further, the simulation time step would have to be reduced to a fraction of a second so the model would not only be much larger but computer runs would be much costlier.

TABLE 1.2-1 SIMWEST LIBRARY COMPONENTS

<u>PHYSICAL</u>		<u>ENVIRONMENTAL</u>	
WIND TURBINE	WT	WIND	WD
TURBINE/GENERATOR	WP	AMBIENT TEMP	TP
AC INDUCTION GEN.	GE		
FIXED RATIO TRANSMISSION	GR	<u>LOAD</u>	
RECTIFIER	RE	ELECTRICAL LOAD	LO
BATTERY	BA	THERMAL LOAD	TL
INVERTER	IV		
ADMITTANCE	AD	<u>LOGIC</u>	
COMPRESSOR (PNEUMATIC)	CO	POWER DIVIDER	PD
ADIABATIC HEAT EXCHANGER (INPUT CYCLE)	HX	POWER ACCUMULATOR	PA
ADIABATIC HEAT EXCHANGER (OUTPUT CYCLE)	HY	PRIORITY INTERRUPT	PI
PNEUMATIC STORAGE VESSEL	CS	SWITCH	SW,SX,SY,SZ
BURNER	BN	<u>UTILITY</u>	
TURBINE (PNEUMATIC)	TU	COST MONITOR	CM
INDUCTION MOTOR	MO	SATURATION	SA
VARIABLE RATIO TRANSMISSION	TR	RANDOM NUMBER GENERATOR	RN
FLYWHEEL/CLUTCH	FL	TEST FUNCTIONS	AF
PUMP (HYDRO)	PU	TABLE LOOKUP	FU,FV
TURBINE (HYDRO)	HT	TRANSFER FUNCTION	IT,LA,LL,TF
HYDRO STORAGE	HS	ARITHMETIC ELEMENT	MA,MB,MC
THERMAL STORAGE	TS	HISTOGRAM	HG
UTILITY	UT	TAPE READ	TA
		TIME CONVERSION	TI

Environmental components are those which simulate environmental conditions. In the present SIMWEST library these conditions are wind speed and ambient temperature. These variables are generally used as inputs to physical components. Environmental component output can either be computed from measurement data provided by the user on a data tape, or from randomly generated data, based on user furnished profiles.

The load components in the SIMWEST library are used to simulate various types of power demand. They also monitor how well the system meets the simulated demand and compute the value of the energy delivered by the wind energy system to the load. Like the environmental components these components may be computed from actual measurement data or from randomly generated data based on user furnished load profiles.

The library's logical components are the power dividers, power accumulators, switches and priority interrupts. Although physical hardware could generally be built to serve the function of the logical components, they are not meant to represent any particular piece of existing hardware. Instead, they are idealized components that allow the user the flexibility of modeling the wide variety of control logic which is required for a thorough evaluation of wind energy storage systems. In practice, the control function might be performed by a control room operator using a predefined control strategy or by use of a minicomputer.

Finally, the utility components include such things as the tape read, the histogram and the cost monitor. These components serve only to help the user run the simulation and analyze its results.

1.2.1 Storage Subsystems

Figures 1.2-1 through 1.2-5 give possible configurations of the five types of storage subsystems which can be modeled with the present SIMWEST library. For illustrative purposes the number of variables shown passed between components is limited. A description of the variables being passed is given in Table 1.2-2.

FIGURE 1.2-1 PNEUMATIC STORAGE SUBSYSTEM

FIGURE 1.2-2 PUMPED HYDRO STORAGE SUBSYSTEM

FIGURE 1.2.3 FLYWHEEL STORAGE

FIGURE 1.2.4 BATTERY STORAGE

LD - LOAD DELIVERED

FIGURE 1.2-5 THERMAL STORAGE

TABLE 1.2-2 PARTIAL LIST OF COMPONENT INPUTS AND OUTPUTS

	<u>SYMBOLS</u>
P	POWER
RE	POWER REQUEST
MP	MAXIMUM POWER
RS	ROTOR SPEED
T	TEMPERATURE
TA	AMBIENT TEMPERATURE
M	MASS FLOW RATE
H	RESERVOIR HEIGHT
LD	THERMAL LOAD DELIVERED
WV	WIND VELOCITY
GR	GEAR RATIO
EF	EFFICIENCY
INT	INTERRUPT FLAG
TSO	MINIMUM AIR TEMPERATURE
PR	PRESSURE
PS	PRIORITY SEQUENCE
WY	WEEK OF YEAR
DW	DAY OF WEEK
TD	TIME OF DAY
SP	SURPLUS POWER
VAR	FILE READ VARIABLE

A total wind energy system will generally be made up of elements from a number of different subsystems (see Figure 2.1-1). In addition, the SIMWEST program can be used for models which include networks of storage subsystems of the same type or a network of wind generators.

1.2.2 Logic Components

The capability for modeling complex system control logic is provided by the power divider, power accumulator and priority interrupt components. Both the divider and accumulator operate on a priority basis. The priority interrupt is used by other system components to change the priority setting of the divider and accumulator.

The power divider has one input power port and four output power ports (not all output ports need be used for a given simulation). The divider also has an input request associated with each of its output power ports. These power requests generally come from a component with which the output power port is directly or indirectly connected. The user specifies priorities of either 0, 1, 2, 3, or 4 to be associated with each of the output ports. If the input power to the power divider exceeds that requested of the port with highest priority (priority 1) then the excess power goes to the port with the next lower priority. This process continues until either all power is distributed or all requests of non-zero priority ports are met. A port with zero (0) priority will never receive power. Such ports are included so that the port may be connected to a component but transmit power only in critical situations, say, when a battery has been in discharge state for a critical amount of time. In these situations, the connected component would have to change the zero priority setting of the power divider by use of a priority interrupt.

Two or more ports may be assigned the same priority in which case the user may specify weights to be associated with each port. Then, if there is not enough power available to satisfy all requests of equal priority, the power is divided between them in proportion to the user specified weights.

The power accumulator is similar to the divider except that instead of distributing power from a single input port between four output ports, it accumulates power from four input ports and sends it out through a single output port. The power accumulator also accepts output power requests from the component connected to its single output power port and it outputs requests for each of its input ports in order to service the output power request.

In addition to the actual power delivered to each input port, the power accumulator also accepts information as to the maximum power that can be delivered to that port. These values are used by the accumulator to determine how to distribute its power request between its four input ports. If the input power request exceeds the maximum deliverable power for the port of highest priority, then the remainder is shifted to the port with the next lower priority. This process continues until either the power request has been completely distributed between the highest priority input ports or all input ports have requests equal to their maximum deliverable power. An example illustration of the use of power dividers and power accumulators is given in Figure 1.2-6. It is seen that power from the turbine/generator is distributed with highest priority (priority 1) going to the power accumulator that services load 1. Since the power accumulator servicing load 1 has its priority 1 input port connected to the power divider, it will try first to satisfy load 1 from the turbine/generator and then from the utility. Thus, if power from the turbine/generator does not exceed that required by load 1, all power will flow to load 1. If there is power left over, it will be used to satisfy the request from the battery. Finally, if the battery is full or if its charging rate is met, then the excess power goes to the flywheel. The battery is connected (through the rectifier) to the wind turbine and also has a priority zero connection to the utility. Thus, if the battery remains in a discharge state for more than a specified amount of time, it can change the utility priority (from 0 to 1) to receive the needed power.

FIGURE 1.2-6 EXAMPLE OF POWER DIVIDER & ACCUMULATOR USE

Also in Figure 1.2-6, we see that load 2 prefers to draw power from the flywheel before turning to the battery. This configuration tends to keep the flywheel as discharged as possible, using it primarily as a means to absorb large influxes of power.

Figure 1.2-6 is a rather simple configuration used for illustrative purposes. A more complex configuration is shown in Figure 2.1-1.

1.2.3 SIMWEST Output

There are three basic forms of SIMWEST output to facilitate the analysis of wind energy storage systems; line printer plots, histograms of system variables and time sequenced output of variable values. To enhance the usefulness of these outputs, each SIMWEST library component is associated with a number of output variables. Prior to simulating a given system the user may select to have the independent variable be time or any of the other variables. For example, he may want to plot the energy of pneumatic storage as a function of time and/or as a function of temperature. If the user wants a time sequenced listing of all variable values, he just specifies the time step between print-outs. The listing of all variables has proven to be a useful tool in understanding the performance of the storage system under consideration and a valuable aid in validating the system design.

1.3 TESTING

Sections 2 and 3 describe two simulation studies which were defined by NASA-Lewis to test the SIMWEST program. They provide an excellent test of its ability to model complex systems and in particular complex control logic. The simulation studies also test the usefulness of the program for doing in depth parameter studies and provide a means for checking the accuracy of the program by comparing simulation results with available empirical data and with the results of other studies.

Prior to performing the simulation studies and throughout its development the SIMWEST program was systematically tested. First components were grouped into simple systems and simulations were performed. During these simulations various system parameters were driven so as to force the individual components through every normal program path and to assure that all component outputs assume a wide range of values. The number of components and the number of ways they can be connected makes it impossible to exercise every combination, however, the subsystem groupings that were used were representative of the expected program usage.

Before the testing, the biggest unknown in the SIMWEST definition was the impact of the logic components (power dividers, power accumulators, etc.) on system convergence. Use of these logic components gives the user considerable flexibility in specifying system logic and every effort was made to minimize their effect on system convergence. All physical components output special information variables which have the sole purpose of speeding the convergence of control logic variables. However, it was still extremely difficult to estimate, apriori what the results of such components would be, particularly with regard to complex systems. Thus, it was particularly reassuring to find that even on very complex systems, such as represented by the NASA-Lewis test case, convergence of logic variables was quite rapid. Convergence generally took place in less than six iterations per simulation time step.

A key requirement of the SIMWEST program was that the amount of training required for its use be minimal. Considerable effort has been made to ensure this is the case. That this is indeed the case is evident by the fact that the two NASA defined simulation tests were performed by an analyst who had just joined the SIMWEST development team and who had no previous experience with SIMWEST or the original EASY program.

In terms of computer efficiency, it was found during the testing that the program exceeded original expectations. As an example, the year simulations used in the NASA defined parameter study took less than 420 CPU seconds on the CDC 6600. The very complex NASA defined test case involved simulating only a one week period of time. It took less than 50 CPU seconds on the 6600. If this time is used to predict the CPU time for a year simulation and account is taken of the fact that most of the CPU associated with I/O is independent of run length, then one would expect the CPU time required to simulate one year for the test case to be 1680 CPU seconds on the 6600. It is estimated that CPU time on the UNIVAC 1100/40 will be approximately two to three times as great as that on the 6600.

1.4 OBSERVATIONS

During the testing it became obvious that while the user need not be a SIMWEST expert or software specialist to make efficient use of the program, he should thoroughly think through and be familiar with the characteristics of the system he wants to simulate. Component models, if not carefully specified, may perform in unexpected ways. They will perform as they were intended but the user must be careful that what he actually specifies is what he really wants. Further, if the systems logic is not well thought out, the resulting system can become severely out of balance and all subsystems may not be fully utilized. (An example of this is given in the test case described in Section 2.)

A number of useful procedures were developed during the simulation studies. First it was found that when simulating a complex system, it is best to develop and test one storage subsystem at a time. This allows problems or unexpected results to be isolated and understood prior to the introduction of the more complex characteristics associated with the total system.

Further, when making a year simulation run, it is best to break it into twelve monthly simulations. Thus, measures of performance such as plots,

histograms and performance statistics are available on a monthly basis. In addition to giving better visibility of the systems actual performance, this helps limit the job core size. The twelve monthly simulation can be submitted as a single run with the results of a given month acting as initial conditions for the next month. The user only needs to submit new data cards for data which changes from one month to the next.

It was also found during the simulations that the use of FORTRAN Statements in the model definition is very useful for creating special input to system components and for defining parameters to be plotted or statistics to be printed. The use of FORTRAN statements is simple and should be encountered early in SIMWEST applications.

1.5 FUTURE APPLICATION

Although the present application of the SIMWEST program is to wind energy systems, it could be just as advantageously applied to other applications where energy storage might be utilized. Such areas include solar heating and cooling and photovoltaic systems. For these applications additional components representing the photocell, thermal collector, etc. would have to be written, or adapted from existing software and added to the SIMWEST library.

However, most of the required components modeling the total system are presently available in the SIMWEST library. Incorporating solar heating and cooling models and/or photovoltaic models into the SIMWEST program would also allow the analysis of hybrid systems containing different combinations of all three solar energy sources.

The present SIMWEST program has a level of detail consistent with a fifteen minute step size. This is ideal for performing analyses which span time intervals on the order of one year. However, this means that many system components, such as the electrical components, are modeled in terms of their steady state response. The SIMWEST program could also be used to analyze such

things as the response of the wind turbine to wind gusts, the impact of large wind turbines on the frequency and voltage control required by small electric utilities and other highly transient effects. However, to do so would require the addition to the SIMWEST library of more detailed component models, particularly for the electrical components.

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2.0 TEST CASE

The first of the two NASA defined simulation studies is described below. It is a "test case" of a relatively complex wind energy system containing five different storage subsystems and three separate loads. It was defined to demonstrate SIMWEST's flexibility and ease of handling complex systems. The other NASA defined simulation study is described in Section 3.

2.1 SYSTEMS OVERVIEW

A schematic diagram of the test case is given in Figure 2.1-1. It contains all five types of storage subsystems available in the SIMWEST library and three separate load components. The wind turbine being modeled has a blade diameter of 48.76 meters (160 feet). It is designed for a mean wind speed of 9.39 meters/sec. (21 mph). The cut in speed and rated speed are 2.68 m/s (6 mph) and 12.67 m/s (28.35 mph) respectively. Rated power of the turbine generator is 790 kw. Wind speeds were randomly generated during the simulation using the random component density function shown in Figure 2.1-2 and a mean daily component profile shown in Figure 2.1-3. The average total load on the system is 264 kw. It is made up of controls, domestic, and thermal loads. The control load is assumed to be constant while the domestic load varies stochastically with the average daily and weekly profiles shown in Figure 2.1-4. The average domestic load is 186 kw. The thermal load varies as a function of ambient temperature and time of day. Its average value is 62 kw. One utility shown in Figure 2.1-1 is labeled as a load but actually it serves only as a place to dump surplus wind energy (when all storage is full) and a means of keeping track of the amount of energy dumped.

FIGURE 2.1-1 SIMWEST TEST CASE

FIGURE 2.1-2 RANDOM WIND COMPONENT DENSITY FUNCTION

FIGURE 2.1-3 WIND DAILY PROFILE

DAILY DOMESTIC LOAD PROFILE

FIGURE 2.1-4 WEEKLY DOMESTIC LOAD PROFILE

The total of all five storage systems has a storage capacity of 11240 kwh. The battery provides 1000 kwh of this, and thus can supply the electrical load for up to 5.37 hours. It can accept energy from the wind turbine at a rate of 80 kw. The storage capacity and power rating of the five storage subsystems is given in Table 2.1-1.

The untitled rectangular components in Figure 2.1-1 represent power dividers and power accumulators. They perform the system control logic and are discussed in detail in Volume II. The power accumulators and dividers are arranged in such a way that the controls load always obtains power from either wind system or from the utility. It has first priority on power from the wind. When power output from the wind exceeds that required by the controls load, excess power goes first to the domestic load and then to the battery. If excess power exceeds the charge rate of the battery, the remainder goes to the flywheel, pneumatic storage, thermal storage and pumped hydro storage, in that order of priority. When all storage systems are full, excess power goes to the utility.

The above described set of storage priorities are established by specifying priority number for each port of the power divider and power accumulator. However, any storage device has the capability of temporarily changing these priorities if it deems it necessary to keep it in the proper operating state. For example, after the battery has been in a discharged state for a specified interval of time, it must obtain power to avoid internal damage.

2.2 TEST CASE SPECIFICATION

The input data for the SIMWEST model generation program is given in Figure 2.2-1. These cards set up the topology of the system to be simulated, and specify the connections between the model components. They do not specify individual component characteristics such as capacities, maximum charging rates, etc. The data creates a Fortran model which contains 50 components, uses 20 lookup tables, and has over 800 input and output variables.

TABLE 2.1-1 CHARACTERISTICS OF STORAGE SUBSYSTEMS

Storage Subsystems	Rated Power (kw)	Capacity (kwh)
battery	80	1000
flywheel	400	400
pneumatic	94	3820
thermal	200	2880
hydro	188	3140

MODEL DESCRIPTION	INTEGRATED TEST CASE	
LOCATION=31	TI	
LOCATION=2	WD	INPUTS=TI
LOCATION=32	WT	INPUTS=WD
LOCATION=52	GR	INPUTS=WT
LOCATION=46	GE	INPUTS=GR
FORTRAN STATEMENTS		
INTPIS=AMAX1(INTFL,INTTS,INTCS,INTNS)		
LOCATION=4	PIS	
LOCATION=16	PD1	INPUTS=GE(P,2=NP),GE(2,0),PA1(1,1),PA2(1,2), PC(1R,0=RE,3),PIA(2,2),PIS(2,3)
LOCATION=38	UT2	INPUTS=PA1(2,2)
LOCATION=7	UTC	INPUTS=PD1(5P=P,3)
LOCATION=48	UT1	INPUTS=PA1(3,2)
LOCATION=19	PA1	INPUTS=PC2(0,0)
LOCATION=73	PD2	INPUTS=LCC(2,1),PA4(4,2),PA2(4,3)
LOCATION=71	LOC	INPUTS=TI
LOCATION=134	LOO	INPUTS=TI
LOCATION=311	PD5	INPUTS=TS(RL,2=RE,3),PIT(2,3),FL(2E,2=RL,1) HS(4E,2=RE,4),PIH(2,4),CS(4E,2=RE,2) PIC(2,2),PUL(P,3=P,6),PIF(2,1)
LOCATION=262	MO1	INPUTS=PD5(1,1)
LOCATION=212	TRI	INPUTS=MC(1,1),LI(AS=RS,2)
LOCATION=215	FL	INPUTS=TFE,PD4(1R,3=RE)
LOCATION=218	TR0	INPUTS=FL,GE2(AS=RS,2)
LOCATION=268	GE2	INPUTS=TR0
LOCATION=101	PD4	INPUTS=GE2,P(1F(4,1),PIC(4,2)
LOCATION=234	PIF	INPUTS=FL
LOCATION=234	PIG	INPUTS=FL
LOCATION=315	TS	INPUTS=TL,PD5(3,1)
LOCATION=333	PIT	INPUTS=TS
LOCATION=319	TP	INPUTS=TI
LOCATION=317	TL	INPUTS=TP(TA,2=TA),TI
LOCATION=431	PU	INPUTS=PD5(4,1)
LOCATION=433	HS	INPUTS=PU,PA3(2,1)
LOCATION=453	PIH	INPUTS=HS
LOCATION=435	HT	INPUTS=HS
LOCATION=459	GE4	INPUTS=HT
LOCATION=521	MO2	INPUTS=PD5(2,1)
LOCATION=533	TR3	INPUTS=MO2,CO(AS=RS,2)
LOCATION=535	CO	INPUTS=TR3,TP
LOCATION=507	HX	INPUTS=CC,TP,CS
LOCATION=520	CS	INPUTS=HX,PD3(1R,0=RE,1)
LOCATION=539	HY	INPUTS=CS,HX
LOCATION=545	PIC	INPUTS=CS
LOCATION=559	ON	INPUTS=HY(2,1)
LOCATION=555	TU	INPUTS=ON,CS(1P,2=PS),TP
LOCATION=574	GE3	INPUTS=TU
LOCATION=123	PD3	INPUTS=GE3,PIA(2,2),PA2(1R,3=RE,2),PA4(1E,3=RE,1)
LOCATION=121	PA2	INPUTS=PD4(2,2),PD3(P,2=P,3),BA(1R,2=RE,4) PIC(4,3),PIA(2,2),PIB(2,4)
LOCATION=171	RE	INPUTS=PA2
LOCATION=148	BA	INPUTS=RE,PA3(1R,1=RE,1)
LOCATION=154	PIB	INPUTS=BA
LOCATION=143	PIA	INPUTS=BA
LOCATION=156	IV	INPUTS=BA
LOCATION=136	PA3	INPUTS=IV,GE4,PIB(4,1),PIH(4,2)
LOCATION=128	PA4	INPUTS=PD3(P,1=P,3),PD4(1,1),PA3(0,2) LOD(1,3),PIC(4,3),GE3(P,2=NP,3)
LOCATION=371	HGW	INPUTS=GE(P,2=FIN)
LOCATION=372	HGB	INPUTS=BA(PE=FIN)
LOCATION=374	HGT	INPUTS=TL(PC=FIN)
FORTRAN STATEMENTS		
FINHGO=LOC*(P2 IV+1.2=6)/(PC PA4+2.4=0)		
LOCATION=373	HGD	
LOCATION=9	CH	
END OF MODEL		
PRINT		

FIGURE 2.2-1 MODEL GENERATION INPUT DATA

As an aid to the user in validating his topology description, the SIMWEST program generates line printer schematics from the description of Figure 2.2-1. An example of the schematic for one section of the test case is given in Figure 2.2-2.

After the user satisfies himself that the model topology is correct, he specifies the parameters establishing the characteristics of the individual components using simulation data cards. The data cards for the test case are given in Figures 2.2-3 through 2.2-5. In addition to specifying the parameters describing the individual components these cards specify the length and step size of the simulation, the variables to be plotted, and the time points at which all variables will be printed. Since the test case is only intended to demonstrate the flexibility of SIMWEST and its ease of modeling complex systems, the period of time selected for the simulation was one week and the simulation step size was set at one hour. Further, output variables were selected for plotting on the basis of illustrating the different capabilities and the general potential of the plotted output for use in system evaluation.

2.3 SUMMARY OF RESULTS

This section gives a summary of the results obtained from the simulation of the test case shown in Figure 2.1-1. One should be cautioned about drawing conclusions from these results. The test case was selected to demonstrate the use of the program and is not necessarily a realistic or rational design from the standpoint of making optimal use of storage subsystems. Furthermore, the simulation covers only a one week period, and therefore the resulting statistics may not be representative.

2.3.1 Wind Power

Figure 2.3-1 gives the histogram of the wind speed that was generated during the simulation. It is seen that the average wind speed is 8.61 meters/sec. (19.25 mph). This is .78 m/s (1.75 mph) lower than that for which the rotor

[illegible]

```

PARAMETER VALUES
MP3PA3=0,MP4PA3=0,MP PDS=1.E8,EF PDS=1
CR CM=18.,LE CM=20.
PS1PI5=3
CYCLES=6.31,OLINES=-10.
VO WT=21,BR WT=87,EC WT=1,CPMWT=.41,CC WT=1eJW,CM WT=500
MP1GR=1.E3,FF1GR=1,CC GR=132,CM GR=9
RAPGE=2000,CC GE=1000,CM GE=50
BS UT2=7,CB UT2=.916,MP1UT2=1.EH,CP UT2=.032,CC UT2=0,CM UT2=0
BS UTD=7,CB UTD=.916,MP1UTD=1.EH,CP UTD=.032,CC UTD=0,CM UTD=0
BS UT1=7,CB UT1=.916,MP1UT1=1.E4,P UT1=3,CP UT1=.03,CC UT1=200,CM UT1=50
SF1A1=1,SF2PA1=1,SF3PA1=1,SF1PA4=1
RAPRE=200,CC RE=200
LC1LOC=15.,VE LOC=0.
FLOHGV=.1,FUPHGV=640.01
FLCHG3=100.,FUPH3=1060.,FLOHGT=0.,FUPHGT=100.,FLCHGD=0.,FUPHGD=10.
VO BA=100,RAPBA=80,E1 BA=100,EOEBA=100,OT BA=10,CC BA=200,CM BA=100
PS1FIA=2,PS1PIB=0,PS3PIB=1
RAPJV=200,CC IV=0
NC LOD=.016,CT LOD=4,MH LOD=0,STDLOD=7,VE LOD=.023
RS P01=1757,RAPM01=1000,CC M01=500,CM M01=0
RS1TR1=1757,CC TR1=100,CM TR1=0
PR FL=.02,MH FL=3372,RF FL=3.4,SR FL=.4,WT FL=2400,KF FL=1.3E-5,ZE FL=.1
CZ FL=0
RAPFL=400,EO FL=40,ET FL=400,EOEFL=20,CM FL=300,CC FL=2000
CC TR0=100,CM TR0=0
RAPGE2=2000,CC GE2=1000,CM GE2=50
PS1FIF=1.,PS3PIH=2.
TS TS=10,VJ TS=11,PD TS=100,MFMTS=10000,LE TS=30,DH TS=.05
TO1TS=200,TO2TS=100,TN1TS=800,TOETS=40
PS1PIF=3.
VE TL=.023,NC TL=40
CT TP=12,MH TP=0,STDTP=5
H1 FU=234
AS HS=36.5,MOPHS=80,MO HS=4.E5,H1 HS=200,MOEHS=4.E5,LE HS=30
CM HS=1000
PS1PIH=4.,PS3PIH=2.
RAPGE4=2000,CC GE4=1000,CM GE4=50
RS M02=1757,RAPM02=1000,CC M02=500,CM M02=0
RS1TR3=1750,CC TR3=100,CM TR3=0
ST HX=32,SE HX=.071,PD HX=150,TEMHX=350,H HX=0,TNTHX=700,L HX=12,LE HX=30
LF CS=30,NU CS=.003,MUFCS=1.E4,PD CS=4500,TN CS=125,TEMCS=350,CM CS=100
PS1PIC=2.,PS3PIC=3.
T3 BN=600,LE BN=30
RAPGE3=2000,CC GE3=1000,CM GE3=50
TABLE,PLOTR1=5,4
3.5,1,1.5,1.72
3.40,907,110,1300
0.15,10,10.5,20
0.10,11,11.5,12
3.10,10,10.5,11
0.6,5.5,7,10
TABLE,PLOTRD=5,4
3.5,1,1.5,1.72
3.40,907,110,1300
0.15,10,10.5,20
0.10,11,11.5,12
0.10,10,10.5,11
3.6,6.5,7,10
TABLE,CLOFL=3,3
-1000, 0, 1000

```

FIGURE 2.2-3 TEST CASE DATA CARDS (PART 1)

```

2000,4000,7000
2.8, 7.4, 15
.9, 2.5, 5
2.6, 7.2, 15
TABLE, CLIFL=3
1000,4000,7000
.147, 2.4, 4
TABLE, PY W0=13
3.,4.33,8.57,13.,17.33,21.67,26.,30.33,34.67,39.,43.33,47.67,52.
65,67,68,69,61,56,51,49,49,52,56,61,65
TABLE, PD W0=7
0,4,8,12,15,21,24
9.33,17,11.67,13.33,11.67,14,8.33
TABLE, DF W0=16
3,1,2,3,4,5,6,7,8,9,10,11,12,13,14,15
5,44,150,390,490,512,440,375,307,270,148,76,46,22,9,3
TABLE, PD L00=17
0,1.5,3,4.5,6,7.5,9,10.5,12
13.5,15,16.5,18,19.5,21,22.5,24
450,363,372,330,450,660,810,758,804
540,708,699,702,790,718,570,450
TABLE, PM L00=7
1,2,3,4,5,6,7
1,1,.9,.9,.9,.6,.5
TABLE, PY L00=6
0,10,20,30,40,52
226,194,180,174,194,226
TABLE, PLOGR=3
10,50,130
.15,.6,1.3
TABLE, HY TS=6
.0147,.0045,.0021,.0009,.1115,.1925
200,565,565,610,611,850
TABLE, PD LOC=17
0,1.5,3,4.5,6,7.5,9,10.5,12
13.5,15,16.5,18,19.5,21,22.5,24
450,363,372,330,450,660,810,758,804
690,708,699,702,790,718,570,450
TABLE, PM LOC=7
1,2,3,4,5,6,7
1,1,.9,.9,.9,.6,.5
TABLE, PY LOC=6
0,10,20,30,40,52
226,194,180,174,194,226
TABLE, PLOTR3=5,4
0.5,1,1.5,1.72
0,400,900,1100,1300
0,16,18,18.5,20
0,10,11,11.5,12
0,10,10,10.5,11
0,6,6.5,7,10
TABLE, ILDTL=4
0,32,60,100
4.,2.,1.5,1.
TABLE, TWITL=4
0,6,18,24
.4,1.,1.,.4
TABLE, PD TP=0
0,3,6,9,12,15,18,21,24
46,45,48,55,62,64,56,48,46
TABLE, PY TP=5

```

FIGURE 2.2-4 TEST CASE DATA CARDS (PART 2)

```

0,13,26,39,52
40,53,75,88,40
INITIAL CONDITIONS, KE FL=380,E CS=370,MS CS=3,3E5,EC1HX=2640,EC2HX=1730
MA MS=1.6E6,E TS=400,PE BA=900
PRINTER PLOTS, PLOT ON
DISPLAY1
PE BA,VS,TIME
E TS,VS,TIME
MA MS,VS,TIME
E CS,VS,TIME
KE FL,VS,TIME
PLOT OFF
DISPLAY2
T2 CS,VS,TIME
INTCS,VS,TIME,YRANGE=-5,5
P2 GE,VS,TIME
P1 PDS,VS,P2 GE
P1 PDS,VS,PE BA
DISPLAY3
FD 3N,VS,TIME
T2 HX,VS,M2 HX
RE1LOD,VS,TIME
RE 1L,VS,TIME
P2 GE,VS,WV2WD
DISPLAY4
LO2LOD,VS,TIME
RE TL,VS,TIME
WV2WD,VS,TIME
TINC=1.,TMAX=168.,PRATE=16,PRINT CONTROL=3,INT MODE=3,CUTRATE=2
TITLE=INTEGRATED SYSTEM MODEL TEST
SIMULATE

```

FIGURE 2.2-5 TEST CASE DATA CARDS (PART 3)

FIGURE 2.3-1 WIND SPEED HISTOGRAM (MPH)

was designed. Figure 2.3-2 is a histogram of the power that resulted from the wind. The mean power is 277 kw. This compares with an average total load of 264 kw. Figure 2.3-3 plots the power generated vs. wind speed. It is seen that at times the power reaches the rated value of 790 kw (when the wind is in excess of 28 mph).

2.3.2 Storage Subsystems

The one week time histories of the five storage subsystems are given in Figure 2.3-4. Notice that the scale on the abscissa should be multiplied by ten to get hours. On the other hand, the scales on the ordinates each have their own multiplicative factor. Thus, for example, the scale for the battery has a maximum of 1000 kwh. From Figure 2.3-4 it is seen that, in general, storage is drained during mid week and builds back up on the weekend. As one would expect, the flywheel shows large fluctuations. This is due to its ability to absorb energy at a high rate and to being the first priority energy source for the domestic load. The battery on the other hand has a lower charge rate but is a second priority source for the domestic load. Thus it remains pretty much in a discharged state during the week. This seems to indicate that the overall control philosophy should be adjusted. The hydro storage tends to discharge its initial charge the first day of operation and is never able to build back up even on the weekend. This can be attributed to the fact that it has the lowest priority of all storage subsystems for charging but has a relatively high priority for discharging.

Figures 2.3-5 through 2.3-7 gives the temperature of the pneumatic storage vessel, the fuel consumption rate of the burner and the outlet temperature of the heat exchanger. Plots such as these are not only useful in monitoring system performance but are also valuable in validating the system definition. It is also useful to make cross plots between different output variables. A cross plot of the power into the flywheel versus the power output by the wind and the battery state of charge is given in Figure 2.3-8 and Figure 2.3-9, respectively. As one would expect, there is good correlation between the wind

FIGURE 2.3-2 WIND POWER HISTOGRAM (KW)

INTEGRATED SYSTEM MODEL TEST

FIGURE 2.3-3 GENERATOR POWER (MW) VS WIND SPEED (MPH)

FIGURE 2.3-4 STORAGE STATE (KWH) VS TIME FOR FIVE STORAGE SUBSYSTEMS

INTEGRATED SYSTEM MODEL TEST

FIGURE 2.3-5 TEMPERATURE OF HEAT EXCHANGER OUTLET

INTEGRATED SYSTEM MODEL TEST

BCS 40180-1

77/09/06.

15.04.26.

SIMULATION DISPLAY 2

CASE NO. 1

FIGURE 2.3-6 BURNER FUEL CONSUMPTION RATE (LB/HR)

4

INTEGRATED SYSTEM MODEL TEST

FIGURE 2.3-7 TEMPERATURE (°F) OF PNEUMATIC STORAGE

BCS 40180-1

INTEGRATED SYSTEM MODEL TEST

FIGURE 2.3-8 POWER INTO FLYWHEEL (KW) VS POWER GENERATED BY WIND

INTEGRATED SYSTEM MODEL TEST

42

BCS 40180-1

77/09/06. 15.05.26.

SIMULATION DISPLAY 1

CASE NO. 1

FIGURE 2.3-9 POWER INTO FLYWHEEL (KW) VS BATTERY STATE OF CHARGE (KWH)

output power and input to the flywheel. However, there seems to be less correlation between the battery state and power into the flywheel. This is primarily due to the fact that the battery was fully charged only a small amount of the time and only in the nearly charged state would one expect to find good correlation.

2.3.3 Load Service

Table 2.3-1 gives the percent of each load met by the various storage subsystems and by the wind directly. In summary, 84 percent of the total load is met by wind generated power. In considering Table 2.3-1, it should be remembered that the domestic load is by far the larger of the three (see Section 2.2-1). About 91 percent of this load is met by wind generated power and nearly 50 percent of this is supplied by the flywheel alone while only 15 percent is met by the battery. When one considers that the flywheel obtains power only when the charge rate of the battery is exceeded, this tends to substantiate the results of the last section which indicate the battery charging rate might be too small. Figures 2.3-10 and 2.3-11 give the frequency histograms of the percentage of the domestic load met by the battery and the flywheel respectively. It is seen that 53.7 percent of the time the battery supplies no power at all to the domestic load. On the other hand the flywheel supplies over 96 percent of the domestic load 18 percent of the time.

Table 2.3-1 also points out that only a small amount of the domestic load was met directly by the wind turbine without going through storage. This is due to the fact that direct wind power is given the lowest priority on the power accumulator supplying the domestic load. This control strategy was mainly selected to exercise the storage subsystems without a great deal of priority given to overall system efficiency.

The actual storage subsystem efficiencies which were obtained during this one week simulation are given in Table 2.3-2. Again the reader should be cautioned about drawing conclusions from these results. In particular, pneumatic

storage, which has one of the lower efficiencies, supplied only 1.5 percent of the total domestic load, and since the simulation only ran for one week, there was not enough data to obtain accurate statistics.

TABLE 2.3-1 LOAD SERVICE BREAKDOWN

Storage Subsystem	Control	Domestic	Thermal
battery	0	15.1	0
flywheel	0	49.1	0
pneumatic	0	1.5	0
thermal	0	0	58.4
pumped hydro	0	9.7	0
direct wind	74.5	18.3	0
utility	25.5	6.3	0
Total	100%	100%	58.4%

84 percent of total load met by wind-generated power.

FIGURE 2.3-10 PERCENTAGE OF DOMESTIC LOAD MET BY BATTERY

FIGURE 2.3-11 PERCENTAGE OF DOMESTIC LOAD MET BY FLYWHEEL

TABLE 2.3-2 STORAGE SUBSYSTEM EFFICIENCY

Storage Subsystem	Round Trip* Efficiency
battery	.94
flywheel	.79
pneumatic	.70
thermal	.86
hydro	.66

* $\frac{\text{total energy in}}{\text{total energy out}}$

3.0 PARAMETRIC STUDY

The parametric study described in this section is the second simulation study defined by NASA-Lewis as a test for the SIMWEST program. It is based upon an energy storage system planned for the NASA-Lewis Plumbrook wind turbine facility. Specifically, this study was intended to assess the accuracy of the SIMWEST program and its usefulness in performing parameter investigations. The Plumbrook facility was felt to be appropriate since empirical performance and cost data is available, and because it has been the subject of other studies with which the results of this study could be compared.

3.1 STUDY OVERVIEW

A schematic diagram of the system to be studied is given in Figure 3.1-1. The wind turbine shown there has a blade radius of 19.05 meters (62.5 ft.) with a cut in wind speed of 4.02 meter/sec (9 mph). The rated wind speed is 8.05 meters/sec (18 mph) beyond which the turbine power output is a constant 100 kw (the rated power). (Wind turbine data from references [1] and [2] were used in this study.)

Unlike the test case described previously, the parametric study used actual wind data. This was hourly data measured at the Plumbrook site during the 1972 calendar year.

The nominal load for the parametric study is 10 kw with lighting making up 70 percent of this and thermal making up 30 percent. In addition, there is a control load of .5 kw which is supplied only when the turbine is operating.

FIGURE 3.1-1 PLUMBROOK CONFIGURATION FOR PARAMETRIC STUDY

Supplying these loads are two storage subsystems, a battery and a thermal unit with the battery accounting for 82 percent of the total storage capacity.

The logic components of Figure 3.1-1 (power dividers and power accumulators) are configured in such a way that the control load gets first priority of the wind generated power. The lighting load has second priority and after that excess power goes to the battery and to the thermal vessel, in that order of priority. If there is still excess power, the surplus power is sold to the utility.

The lighting load requests power first directly from the turbine. If the turbine cannot completely satisfy the load, it turns next to the battery, and finally if the load is still not met it receives power from the utility network. Similarly the controls load first requests power from the wind turbine, and if it is not met it next turns to the utility network. The thermal load is supplied only by the thermal storage unit.

The primary system parameters to be varied in this study are the size of the lighting and thermal loads (their sum taking the values of 10, 20, and 30 kw), the total system storage capacity (2 hours, 4 day and 15 day supply of the load), the wind cut in speed (9 and 10 mph), the initial state of charge of the storage subsystems, and the inverter configuration. It is known that inverters function most efficiently near their rated capacity. The study will determine whether using two inverters is more efficient than using one inverter of twice the size.

A single case having a 10 kw load, 4 days of storage, 9 mph cut in speed, and one inverter is used as nominal and each of the parameters are sequentially varied keeping the remainder of the parameters at their nominal values. It should be pointed out that every separate set of parameters requires a separate simulation (although a number of simulations can be made in one computer run). A summary description of critical parameters is given in Section 3.6.

3.2 BATTERY SUBSYSTEM

The subsystem consists of a rectifier, an inverter (or two) and a number of battery cell banks. The charge-discharge characteristic of each cell bank is given in Figure 3.2-1.* Each cell bank has an average terminal voltage of 120 volts and a storage capacity of 20 kwh. The study assumes as many cell banks, in parallel, as needed to give the desired total storage capacity. Using the SIMWEST battery component each battery cell bank is modeled mathematically as a capacitance, a terminal resistance, and an internal voltage. See Figure 3.2-2.

FIGURE 3.2-2 BATTERY MODEL

The capacitance and internal voltage for a single bank are 49505 Farads and 115.2 volts respectively. The terminal resistance varies with current and state of charge, resulting in the characteristic curves in Figure 3.2-1. Likewise, the internal resistance varies so as to reduce by 4.8 percent the charging current. This models a 95.2% amp-hr. charging efficiency. When the battery is not charging, the internal resistance reduces to a constant leakage resistance which allows leakage of half of the storage in one month. The terminal resistance is modeled by a table lookup while the internal resistance is computed using a FORTRAN statement.

* Characteristic curves obtained from Reference [3].

FIGURE 3.2-1 BATTERY CELL VOLTAGE CHARACTERISTICS

For the nominal case of a 10 kw load and a four day storage supply, the battery can store $10 \times 4 \times 24 \times .82 = 787.2$ kwh. Thus about 39 banks (of 60 cells each) were used in the simulation. The rated input and output power for all battery sizes studied are 30 kw. However, the rated input power to the inverter is 10 kw. Thus the effective discharge rate of the battery is 10 kw.

When the battery remains in a discharged state in excess of twelve hours, it will cause the system logic to change priorities so that it purchases power from the utility until its storage level reaches 50 kwh. The model's rectifier and inverter efficiencies varies with the load. Their efficiencies as a function of percent load are shown in Figure 3.2-3.* The rectifier and inverter for the nominal case have rated power = 30 kw and 10 kw respectively.

3.3 THE THERMAL SUBSYSTEM

Anhydrous sodium hydroxide is used as a heat storage medium, with phase changes occurring at 296.11°C (565°F) and 321.11°C (610°F). Maximum and minimum storage temperatures are 454.44°C (850°F) and 232.22°C (450°F) respectively. Whenever the temperature falls below 500°F , the thermal vessel will change the system's logic so that power can be purchased from the utility until the temperature rises to 510°F . The storage media mass is chosen in such a way that the maximum stored energy corresponds to a temperature of 343.33°C (650°F). Thus in the nominal case where 172.8 kwh storage capacity is desired, it is found from the enthalpy-temperature curve (see Figure 3.3-1) of sodium hydroxide that 662.24 kg (1460 lb) are needed. This design point enthalpy is .088 kwh/lb, corresponding to a design point temperature of 313°C (595°F). Thus $1460 \times .088 = 128$ kwh are stored at the design point. This corresponds to a rated storage time of 4.28 hours assuming a rated (design point) power of 30 kw. The rated storage time is the only parameter which needs be changed to give different storage capacities from simulation to simulation.

* See Reference [4].

FIGURE 3.2-3 RECTIFIER AND INVERTER EFFICIENCIES

FIGURE 3.3-1 TEMPERATURE-ENTHALPY CURVE FOR THERMAL VESSEL HEAT STORAGE MEDIA

3.4 PARAMETRIC STUDY SPECIFICATION

The input cards for the SIMWEST model generation program used for the parametric study are given in Figure 3.4-1. These cards define the general topology of the system shown in Figure 3.1-1. The schematic printout of the resulting system is shown in Figures 3.4-2 through 3.4-4. Figure 3.4-2 shows the portion of the system which contains the wind turbine and the utilities. Figure 3.4-3 shows the battery subsystem. Figure 3.4-4 depicts the thermal subsystem as well as the cost monitor and the histogram components. In Figure 3.4-2, the wind turbine WT drives the generator GE through the gear GR according to time TI and wind data WD. The power is then distributed by the power divider PD1. Note that PD1 receives requests from the power accumulator PA3 in the thermal system shown in Figure 3.4-4. Likewise, the power divider PD2 receives requests from, and supplies, the power accumulator PA2 in Figure 3.4-3. Communication with a component printed on a different page is depicted by the input name and page number of the component. Thus, the request RE2PA2 together with PAGE 1 is printed at the lower left of PD2 in Figure 3.4-2.

Each simulation of the parametric study required a slightly different set of simulation data cards. The set of data cards used for the nominal system is given in Figure 3.4-5. In the parametric study wind data was also input through simulation data cards. For brevity these are not included in Figure 3.4-5. A summary description of the more important parameters is given in the appendix.

3.5 SUMMARY OF RESULTS

Figure 3.5-1 gives the average output power from the wind turbine generator which would be generated by the 1972 Plumbrook wind data. It is seen that the power drops off significantly during the summer months. The average output power over the twelve month period is 20 kw. During the simulations this energy attempts to satisfy combined lighting and electrical loads of 10, 20, and 30 kw. Excess power goes to a battery unit with a charging rate of 58.6 kw.

```

MODEL DESCRIPTION          PARAMETER STUDY
ADD PARAMETERS=           C860, CCBA60, RUBA60, ANBAT, CFACT, CUSTO, COST1
ADD VARIABLES=OPCOST, PCWTL
ADD TABLES=WIND, 802
FORTRAN STATEMENTS
COMMON/CSIMIL/ADUM(6),TINC
LOCATION=41      TI
FORTRAN STATEMENTS
C      READ WIND VELOCITY DATA
WVIND=TBLU2(10 TI,DY TI,WIND(35),WIND(4),WIND(59),
1 0,0,24,-31,24,31)
LOCATION=71      WD      INPUTS=TI
LOCATION=62      FUW      INPUTS=WD(4V,2=FIN)
LOCATION=53      WT      INPUTS=WD,FUW(FO=CP)
FORTRAN STATEMENTS
C      SET GEAR RATIO
GR WT=45.
LOCATION=65      GR      INPUTS=WT
LOCATION=45      GE      INPUTS=GR
LOCATION=23      PIW      INPUTS=GE(P,2=INT)
LOCATION=25      PD1      INPUTS=GE(P,2=MP),GE,PA1(1,1),PA2(1,3),PA3(1,4),
PA4(1,2)
LOCATION=48      UT1      INPUTS=PA1(3,2)
LOCATION=17      UT2      INPUTS=PA1(2,2),PD1(SP=P),FUU(FO=CP)
LOCATION=172     UT3      INPUTS=PA4(4,2),FUU(FO=CP)
LOCATION=28      PA1
LOCATION=10      PD2      INPUTS=PIW(2,1),PA1(0,0),PA2(2,3)
LOCATION=1       LOC      INPUTS=TI,PD2(1,1)
LOCATION=107     PA2      INPUTS=BA(RE,2=RE,0),PIC(2,2)
LOCATION=125     FUR      INPUTS=PA2(P,0=FIN)
LOCATION=133     RE      INPUTS=PA2(0,1),FUR(FO=RR)
FORTRAN STATEMENTS
C      ANBAT IS NUMBER OF 60 CELL STRINGS IN PARALLEL IN BATTERY
C      FVB IS TABLE LOOKUP FOR TERMINAL RESISTANCE OF SINGLE STRING
CC BA=CCBA60*ANBAT
CM BA=CC BA*.04
FNAFVB=1 BA/ANBAT
LOCATION=171     FVB      INPUTS=BA(VC=FNB)
FORTRAN STATEMENTS
CB BA=C860*ANBAT
RT BA=FU FVB/ANBAT
LOCATION=141     BA      INPUTS=RE,PD3(RE,0=RE,1)
LOCATION=147     PIC      INPUTS=BA
LOCATION=153     PD3      INPUTS=BA(2,0),PA4(RE,2=RE,1),PA4(RE,3=RE,2),
FORTRAN STATEMENTS
C      INTERNAL RESISTANCE TO ACCOUNT FOR BATTERY AMP-HR CHARGING EFFICIENCY
RL BA=ROBA60*(VC BA + 1.E-8)/
X (VC BA + 1.E-8 - .048*AMIN(1 BA,0.)*ROBA60)
LOCATION=166     FU1      INPUTS=PD3(P,1=FIN)
LOCATION=164     IV1      INPUTS=PD3(1,1),FJ1(FO=RI)
LOCATION=169     FUJ      INPUTS=PD3(P,2=FIN)
LOCATION=167     IV2      INPUTS=PD3(2,1),FUJ(FO=RI)

```

FIGURE 3.4-1 MODEL GENERATION INPUT DATA

FORTRAN STATEMENTS

MP2PD1=P2 GE - P1 PD1

MP3PD1=MP2PD1 - P2 PD1

MP4PD1=MP3PD1 - P3 PD1

LOCATION=175 PA4 INPUTS=IV1(2,2),IV2(2,3),LOD(1,3)

LOCATION=258 FUJ INPLTS=TI(TD=FIN)

LOCATION=180 LOD INPUTS=TI,FUU(FD=VE)

LOCATION=212 PA3 INPUTS=UT4(2,2),TS(2,0)

LOCATION=242 UT4 INPUTS=FUU(FD=CP)

LOCATION=215 TS INPUTS=TL

LOCATION=218 TL INPUTS=FUU(FD=VE)

FORTRAN STATEMENTS

C RESET PRIORITY FOR POWER PURCHASE WHEN THERMAL VESSEL LOW

PS2PA3=0.

IF(T TS.LE.T01(3))PS2PA3=2.

C HISTOGRAM OF POWER PURCHASE FROM UTILITIES:

C STORAGE SYSTEM IN OPERATION WHEN PURCHASE IS 0

FINHG=P2 UT1 + P2 UT2 + P2 UT3 + P2 UT4

LOCATION=262 HG

FORTRAN STATEMENTS

C COMPUTE PERCENT OF THERMAL LOAD SUPPLIED BY WIND

PCWTL=100.*PCIPA3/(PCIPA3+PC2PA3+1.E-8)

C HISTOGRAMS OF POWER SURPLUS AND POWER PURCHASE COST

C IF NO STORAGE SYSTEM WERE USED

PWSP=P2 GE - (RELOC + RETOD + RE TL*CFAC)

P4PC=AMAX1(-PWSP,0.)

PWSP=AMAX1(PWSP,0.)

FINHGS=PWSP*TINC

FINHGP=PWPC*TINC*FO FUJ

IF(IMPL.EQ.0)COST1=0.

IF(IMPL.LE.1)GO TO 10

COST1=COST1 + .5*FINHGP - .5*FINHGS*CB UT2

C COST0 IS PER HOUR COST (CAPITAL AND MAINTENANCE) OF

C WIND SYSTEM WITHOUT STORAGE

COST0=(CC WT + CC GR + CC GE + CC UT1 + CJAIS*.4*PD IS)*LE CM *

X CR CM*.01/8760. + (CM WT + CM GR + CM GE + CM UT1)/8760.

OPCOST=(COST0*TIME + COST1)/(SRELOD + SRETC + 1.E-8)

10 CONTINUE

LOCATION=263 HGS

LOCATION=264 HGP

LOCATION=265 CM

END OF MODEL

PRINT

FIGURE 3.4-1 MODEL GENERATION INPUT DATA (Cont.)

PARAMETER STUDY										PAGE 0
*****										*****
LOC									RELLOC	P02
1										10
*****										*****
NP1P02										PS2P1
P1 P02										MP0P1
FD T1									*****	
04 T1									*****	
05 T1									*****	
11	12	13	14	15	16	17	18	19	20	
1									REOPD2	
1									*****	
1									*****	
1									*****	
11	22	23	24	25	26	27	28	29	30	
1									*****	
1									*****	
1									*****	
1									*****	
11	32	33	34	35	36	37	38	39	40	
1									*****	
1									*****	
1									*****	
1									*****	
11	52	53	54	55	56	57	58	59	60	
1									*****	
1									*****	
1									*****	
1									*****	
11	62	63	64	65	66	67	68	69	70	
1									*****	
1									*****	
1									*****	
1									*****	
11	72	73	74	75	76	77	78	79	80	
1									*****	
1									*****	
1									*****	
1									*****	

FIGURE 3.4-2 SCHEMATIC PRINTOUT (PAGE 0)

[illegible]

[illegible]

```

PARAMETER VALUES
CR CM=18.,LE CM=10
CFAC=1.
CYCLES=4.01,DI INFS=-10.,RESFT=-1.
TO TI=0.
VD WT=12.,VP WT=18.,PSCWT=100.,RP WT=62.5,EC WT=0.,AD WT=.0023,LAMWT=10.
CPMWT=.45,CC WT=AA000.,CM WT=2640.
EF1GP=.95,MP1GP=1.,CR,CC GR=1500.,CM GR=64
RAPGE=100.,PVGGE=100.,PAGGE=.705,DA GE=0.,SP GE=.0847,VD GE=400.
CC GE=6800.,CM GE=777
CB UT3=.008,CC UT3=0.,CM UT3=0.
CB UT1=0.,MP1UT3=10.,CP UT3=.008,CC UT1=180.,CM UT1=7.2
CB UT2=0.,CC UT2=0.,CM UT2=0.
PSIPID=0.
VE LOC=0.,LOLID=5.,FFLOC=1
VACRE=400.,PAPPF=70.,CC RE=1400.
VO BA=115.2,PAPRA=30.,E1 RA=787.,EDERA=50.,DT BA=12,CCBA60=150
CR60=49505,DRRA60=4.467,ANSAT=39.
PSIPIC=0.,PSPIC=7.
VDCIV1=100,RAPIV1=10,CC IV1=1000
VDCIV2=100,PAPIV2=0.,CC IV2=0.
LOLID=7,EF1LOD=1
CC UT4=0.,CM UT4=0.
NU TS=.002,TS TS=4.293,VO TS=490,TMTS=700,TOLTS=500,DH TS=.087989,PD TS=30.
PM TS=58.6,HEMTS=440,THETS=30,CR2TS=9.49E-4,TO2TS=50,TM2TS=190
R TS=3.08E-4,CM TS=7.467,CS4TS=666.7,CSBTS=6.,LE TS=10
NC TL=3.,AN FUH=-1.,AN FVR=-1.,AN FVR=-1.,AN FUI=-1.,AN FUJ=-1.
AN FUR=-1,AN FUW=-1
FLOHG=.001,FHPHG=140.001
FLOHGS=.001,FHPHGS=94.001
FLOHGP=.001,FHPHGP=.701
TABLE,FTAFUW=10
0.999,9,10,11,12,15,18,25,30,50
0.,28.,34.,375.,4.,47.,45.,37.,25.,095
TABLE,PLOGR=3
0,12,32,138,44
0,12,32,53,44
TABLE,HT TS=6
.0147,.0645,.0821,.0909,.1115,.1525
200,565,565,610,610,850
TABLE,FTAFUU=4
6.999,7,22,72,001
.023,.026,.026,.023
TABLE,FTAFUT=17
.5,1,1.5,2,3,4,5,6,7,8,9,10
16.6,4,9,1.63,.775,.317,.2,.13,.1,.079,.075,.078,.08
TABLE,FTAFUJ=17
.5,1,1.5,2,3,4,5,6,7,8,9,10
16.6,4,9,1.63,.775,.317,.2,.13,.1,.079,.075,.078,.08
TABLE,FTAFUP=9
.075,1.75,3.51,5.26,7.07,10.57,14.17,54,70.16
521,12.5,4.85,2.59,1.59,.795,.519,.344,.0831
TABLE,TLDTL=2
0.,1.
1.,1.
TABLE,TWTL=2
0.,1.
1.,1.
TABLE,FTAFVR=16,4
1.2, 6, 10,8, 17
-280 , -140 , -70 , -34.6 , -17.3 , -8.67 , -3.48 , -1.74 ,
0 , 3.3 , 8.25 , 14.5 , 33 , 66 , 132 , 264 ,
.32 , .64 , .128 , .255 , .485 , .90 , 2.24 , 4.48 ,
1.E-8 , 1.E-8 , .145 , .197 , .154 , .082 , .041 , .02 ,
.0325 , .065 , .13 , .26 , .416 , .69 , 1.2 , 2.4 ,
1.E-8 , 1.E-8 , .073 , .145 , .109 , .055 , .028 , .014 ,
.035 , .07 , .14 , .277 , .164 , .415 , .172 , .344 ,
1.E-8 , 1.E-8 , .073 , .145 , .109 , .055 , .028 , .014 ,
.13 , .26 , .53 , 1.075 , 1.9 , 3.32 , 6.55 , 13.1 ,
1.E-8 , 1.E-8 , .073 , .145 , .109 , .055 , .028 , .014
INITIAL CONDITIONS,PE RA=750,E TS=100
PRINTER PLOTS
DISPLAY1
PF BA,VS,TIME
E TS,VS,TIME
INTBA,VS,TIME,YRANGE=-5,5
INTTS,VS,TIME,YRANGE=-5,5
VT RA,VS,VC RA
DISPLAY2
P2 GE,VS,WVWD
RL RA,VS,VC RA
WVWD,VS,TIME
T TS,VS,E TS
EF2IV1,VS,P1 P01
DISPLAY3
PC2PA4,VS,TIME
PCWTL,VS,TIME
SP PD1,VS,TIME
TINC=1.,THAY=744.,PDATF=49,PRINT CONTROL=3,INT MODE=3,OUTRATE=3
TITLE= PARAMETER STUDY OF STORAGE SYSTEM
SIMULATE=

```

FIGURE 3.4-5 PARAMETRIC STUDY INPUT DATA

FIGURE 3.5-1 AVERAGE WIND TURBINE OUTPUT POWER (KW)

3.5.1 Effect of Load On Cost of Operation

Figure 3.5-2 shows the effect of 3 different load sizes (10, 20, and 30 kw) on the monthly cost of usable energy (whether supplied to the load or sold to the utility); the cost of energy is the sum of all costs (capital, maintenance, and operating) divided by the total amount of wind generated energy that was actually supplied to a load or surplus to the utility. Capital costs are amortized based on a ten year life expectancy. It is seen in Figure 3.5-2 that the cost rises with the size of the load. This is because a four day storage capacity is assumed in each case. Thus, for example, the capital cost for supplying four days of storage for a 30 kw load is greater than that required to supply four days of storage for a 20 kw load.

Returning to Figure 3.5-2, the January energy cost of under 50¢/kwh corresponds to a monthly average wind speed of 6.7 m/s (15 mph) while the cost of above \$3/kwh in July and August results from the fact that the average wind speed for these two months are below 3.67 m/s (8.2 mph).

Another way of looking at the cost of energy is to assume, as is shown in Figure 3.1-1, that the loads must purchase energy from the utility when not supplied by the wind system. If this purchased energy is added to the total energy delivered and the added cost of this energy is added to the total cost of energy, then the resulting cost curves are as shown in Figure 3.5-3. In this study energy was purchased from the utility at 2.6¢/kwh during the peak time from 7 AM to 10 PM and 2.3¢/kwh at off peak times.

In Figure 3.5-3, it is seen that now energy is most expensive in the 10 kw load case. This is because the incremental energy added by the utility in the 30 kw case is larger than that of the 10 kw case, and the added cost in either case is small compared to the total system cost. The situation in Figure 3.5-4 is the same as in 3.5-3 except that the simulation was run without storage.

FIGURE 3.5-2 MONTHLY COST OF WIND GENERATED ENERGY

FIGURE 3.5-3 MONTHLY ENERGY COST TO SATISFY THE LOAD

FIGURE 3.5-4 MONTHLY COST OF ENERGY (WITHOUT STORAGE)

One further observation before leaving the subject of energy cost. For the above two computed costs (with and without buying energy from the utility), it was assumed that the system gets credit for surplus wind power. Thus, the total amount of energy in the cost calculation includes not only energy that was delivered to the load but also energy that was surplus to the utility. If it is assumed that the system does not get credit for this surplus energy and also does not buy power from the utility, then the energy costs should go up. Figure 3.5-5 shows the result of this situation. Again, the order of the curves have reversed themselves from Figure 3.5-2. It is seen that if one does not get credit for surplus energy, the system with the larger load and larger storage capacity produces the cheapest power. Figure 3.5-6 gives the energy cost for the same situation if no energy storage is used. It is seen that in the summer months when the average wind speed is low, cost of energy without storage is roughly twice as high as with storage. While during the winter months the cost without storage is approximately 50% higher.

3.5.2 Effect of Load Size on Frequency of Operation

Figure 3.5-7 exhibits the effect of the three different load sizes on the frequency of operation. The frequency of operation is defined to be the percent of time the wind energy system supplies 100 percent of the load. As before, there are different systems supplying the loads so that for each load the system contains the nominal four days of storage. From Figure 3.5-7, it is seen that during the less windy months the frequency of operation drops. Furthermore, even though the 30 kw load utilizes three times as much storage, the 10 kw load case has a much higher frequency of operation (90% in the winter, 60% in summer). Figure 3.5-8 illustrates the situation when no storage is used. It is seen that for the nominal 10 kw case storage (4 day) increases the frequency of operation by roughly 50 percent in the winter months and 200 percent in the summer months. Furthermore, in each of the twelve months the system with storage fully supplies a 20 kw load more often than the wind turbine alone will supply a 10 kw load, i.e., in terms of frequency of operation adding 4 days storage doubles the effectiveness of the wind turbine.

FIGURE 3.5-5 ENERGY COST WITH NO PURCHASE FROM UTILITY
AND NO CREDIT FOR SURPLUS POWER

FIGURE 3.5-6 ENERGY COST WITH NO PURCHASE FROM UTILITY,
NO CREDIT FOR SURPLUS AND NO STORAGE

FIGURE 3.5-7 EFFECT OF LOAD SIZE ON FREQUENCY OF OPERATION (WITH STORAGE)

FIGURE 3.5-8 EFFECT OF LOAD SIZE ON FREQUENCY OF OPERATION (WITHOUT STORAGE)

3.5.3 Effect of Cut In Speed On Frequency of Operation

The effect of cut in speed on frequency of operation was studied by assuming the transmission generation efficiency was such that the turbine power at cut in speed was just equal to power needed to overcome friction and inertia in the gear/generator drive train and start generating power. Thus, the turbine/generator for the 9 mph cut in speed is assumed to be more efficient than that for the 10 mph cut in speed. This difference in efficiencies decreases with increasing wind velocity until the generator hits rated power. Figure 3.5-9 gives the frequency of operation of two wind turbines with different cut in speeds, 4.02 meters/sec. (9 mph) and 4.47 m/sec. (10 mph). As one might expect, the design with the lower cut in speed generally produces more power. Two exceptions, however, are noted in Figure 3.5.9. In the months of February and April, because 4.02 m/s (9 m/h) winds occur much more frequently than 4.47 m/sec (10 mph) winds, the wind turbine with the lower cut in speed has more marginal operations. During this time the power generated is sufficient to activate the turbine but not sufficient to supply the control load so that a nominal amount of energy is purchased from the utility. As a result, the lower cut in speed actually resulted in a lower frequency of operation.

3.5.4 Effect of Initial State of Storage on Frequency of Operation

Simulations were conducted to determine the sensitivity of the study results to initial state of the storage subsystems. Since the simulations span a years time and the nominal storage capacity is only four days, one would expect the initial condition to have little effect on the overall performance. This was indeed the case. During the first month of the simulation (January), the difference in the frequency of operation between the two cases was negligible. However, there was a 1.76 percent difference in the total amount of energy purchases from the utility. The difference for the following months was even less significant. It might be pointed out that January is a month of relatively high winds. One would expect somewhat greater difference in the

FIGURE 3.5-9 FREQUENCY OF OPERATION FOR DIFFERENT TURBINE CUT-IN SPEEDS

first month performance if the simulation had been started in July rather than January. However, even then these results indicate the effect would be negligible.

3.5.5 Effect of Storage Capacity on Frequency and Cost of Operation

In order to determine the effect of storage capacity on frequency and cost of operation, simulations of three different storage capacities were conducted for each of the three load levels (10, 20, and 30 kw) and also for a time varying load. The three storage capacities were two hours, four days, and fifteen days. The effect of storage on the frequency of operation is summarized in Figure 3.5-10. The percent of operation is computed for the full year. It is seen that for the 10 kw load, increased storage resulted in improved frequency of operation but for a 30 kw load little improvement was achieved. This is due to the fact that the average power from the wind is only 20 kw (see Figure 3.5-1) thus for a constant 30 kw load very little energy goes into storage.

The time varying load of Figure 3.5-10 was produced using the electrical and thermal load profiles shown in Figure 3.5-11. The loads were scaled so that the total average load was 20 kw and 70 percent of the load was electrical. It is interesting to note that for constant loads the percent of operation is generally greater than for time varying loads of equal average value.

The effect of storage on the yearly cost of energy delivered to the load is summarized in Figure 3.5-12. It is seen that by increasing storage size beyond four days supply, one increases capital cost without a commensurate increase in frequency of operation. Figure 3.5-13 gives the yearly costs of energy delivered to the load assuming no utility tie-in. In this case less energy is delivered, resulting in a higher cost per kwh than for 3.5-12.

FIGURE 3.5-10 EFFECT OF STORAGE SIZE ON FREQUENCY OF OPERATION

FIGURE 3.5-11 DAILY LOAD PROFILES

FIGURE 3.5-12 EFFECT OF STORAGE SIZE ON COST OF ENERGY TO LOAD

FIGURE 3.5-13 EFFECT OF STORAGE SIZE ON COST OF ENERGY TO LOAD
(NO UTILITY AVAILABLE)

3.5.6 Study of Inverter Efficiency

A study was performed with two 5 kw inverters replacing the one 10 kw inverter used for the nominal case. It is known that inverter efficiencies improve with the degree of utilization (see Figure 3.2-3). Thus one might expect that, for situations where full utilization of inverter capacity is not common, the use of the two inverters would increase the efficiency of the storage system. To perform this study, it was necessary to change the simulation step size away from the one hour step size used for the rest of the study. This is because the wind data is given only at discrete levels which result in requests to the battery not representative of a spectrum of values. The step size was thus set at 1.9 hours. This required interpolation between wind speed data so that a representative spectrum of power requests were made to the battery.

The frequency of operation using two inverters is compared with that using one in Figure 3.5-14. The results were unexpected in that one full size inverter outperforms the two half size inverters. By calculating the composite efficiency of two inverters, one can understand why this is the case. Figure 3.5-15 compares the two efficiency functions. It is seen that the average efficiency of the two inverter system is the same as that of one inverter. However, the latter has a higher efficiency than the former in the region of high power flow (40% of capacity and higher), where efficiency counts more. Thus, in the long run the one inverter system allows a greater fraction of the input power to flow through. This conclusion is made under the assumption that the input power is uniformly distributed over the capacity range of the inverter, as is the case in this parameter study. If some other distribution is valid, the two inverter system may indeed have better performance.

FIGURE 3.5-14 COMPARISON OF FREQUENCY OF OPERATION
FOR TWO INVERTER SYSTEMS

FIGURE 3.5-15 COMPARISON OF INVERTER EFFICIENCIES

3.6 SUMMARY OF CRITICAL SYSTEM PARAMETERS

In this section, critical parameters are summarized in tabular form. The same parameter names are used as in the analysis command cards.

3.6.1 Wind Turbine-Gear-Generator

VO WT	Design point mean wind speed = 5.37 (12 mph)
VR WT	Rated wind speed = 8.05 (18 mph)
BR WT	Blade radius of turbine = 19.05 meter (62.5 ft.)
LAMWT	Design tip speed ratio = 10
FTAFUW	Wind power coefficient curve (Figure 3.6-1)
CC WT	Capital cost of wind turbine = \$66000 per year
CM WT	Maintenance cost of wind turbine = \$2640 per year
PLOGR	Power loss curve for gear (Figure 3.6-2), designed so that all power below cut-in is lost.
RAPGE	Rated output of generator = 100 kw
DA GE	Generator mechanical damping = 0
SR GE	Generator rotor resistance = .0842 ohm (so that generator has .95 internal efficiency at rated power)

3.6.2 Rectifier-Battery-Inverter

FTAFUR	Rectifier resistance curve (Figure 3.6-3), designed so that rectifier efficiency curve in Figure 19 results.
RAPRE	Rectifier rated input power = 70 kw
CCBA60	Capital cost of one 60 cell bank = \$150
CB60	Capacitance of one 60 cell bank = 49505 farad
FTAFVB	Terminal resistance of one 60 cell bank as function of charge-discharge current and state of charge, designed to produce the charge-discharge characteristics as shown in Figure 3.2-1.

ANBAT	Number of 60 cell banks	} varies from simulation to simulation
EI BA	Battery capacity	
GDEBA	Minimum allowable battery storage	
RAPBA	Rated battery input power = 30 kw	
RAPIV1	Rated inverter input power = 10 kw	
FTAFU1	Inverter resistance curve (Figure 3.6-4) designed so that inverter efficiency curve in Figure 19 results.	

3.6.3 Thermal Vessel

TMITS	Maximum storage temperature = 454.44°C (850°F)
TOITS	Minimum storage temperature = 232.22°C (450°F)
PD TS	Rated storage thermal power = 30 kw
PM TS	Maximum charge rate = 58.6 kw
TS TS	Rated storage time (varies with storage capacity)
HT TS	Enthalpy - temperature curve for storage media (Figure 3.2-4)

3.6.4 Loads

LO1LOD	} Domestic load constants varying from simulation to simulation thermal load
NC TL	

In three of the simulations, the loads vary with time and are supplied by a daily profile (Figure 3.5-11).

FIGURE 3.6-1 TURBINE POWER COEFFICIENT VS. WIND SPEED

FIGURE 3.6-2 GEAR LOSS (kW) VS. INPUT POWER (kW)

FIGURE 3.6-3 CURVE USED FOR RECTIFIER EFFICIENCY

FIGURE 3.6-4 CURVE USED FOR INVERTER EFFICIENCY

4.0 LIST OF REFERENCES

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THIN FILM BATTERY/FUEL CELL POWER GENERATING
SYSTEM

Final Report, Task E4, April 1976—April 1978

March 31, 1978

Work Performed Under Contract No. EY-76-C-03-1197

Research and Development Center
Westinghouse Electric Corporation
Pittsburgh, Pennsylvania

U. S. DEPARTMENT OF ENERGY

Division of Energy Storage Systems

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Thin Film Battery/Fuel Cell Power Generating System

Final Report
Task E4
Covering the Period
April 1976 to April 1978

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Prepared for the United States
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Under Contract No. EY-76-C-03-1197

by

Research and Development Center
WESTINGHOUSE ELECTRIC CORPORATION
Pittsburgh, Pennsylvania 15235

March 31, 1978

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Foreword

For DOE Contract EY-76-C-03-1197, the Department of Energy Program Managers, from Fuel Cell Applied Research, were Mr. I. L. Harry, during the first year, and Mr. R. F. Dudley, during the second year. Their advice and assistance in program planning and in contract-related matters is gratefully acknowledged.

TABLE OF CONTENTS

	<u>Page(s)</u>
1.0 Abstract	xiii-xiv
2.0 Program Summary	1-4
3.0 Introduction	5, 6
4.0 Technical Background	7-15
4.1 How Solid Electrolyte Fuel Cells Generate Electricity	7-11
4.2 Fabrication of Fuel Cell Stacks	11-13
4.3 High-temperature Coal Burning Fuel Cell System	14-15
5.0 The Present Program	16
6.0 Overall Technical Effort	17-170
6.1 Task 1. Materials Identification and Selection	17-45
6.1.1. Subtask 1A. Interconnection Literature Search	17-18
6.1.2. Subtask 1B. Modification of Interconnection Materials	18-45
6.1.2.1. Variation in Oxygen Content of Lanthanum Chromite	19-22
6.1.2.2. Thermal Expansion Studies	22-27
6.1.2.3. Radio Frequency (RF) Sputtering of Interconnection Material	27-45
6.1.2.3.1 Background	27-31
6.1.2.3.2 Technical Approach	31-37
6.1.2.3.3 Experimental Results	37-42
6.1.2.3.4 Heat Treating and SEM Examination of RF Sputtered Film	43-44
6.1.2.3.5 Summary	45
6.1.3. Subtask 1C. Development of Other Stack Components	45-46
6.1.3.1. Fuel Electrode Development	45
6.1.3.2. An Electrode Development	46
6.1.3.3. Solid Oxide Electrolyte Development	46

Table of Contents (Continued)

	<u>Page(s)</u>
6.2 Task 2. Fabrication Techniques	46-118
6.2.1. Subtask 2A. Interconnection Fabrication	46-54
6.2.2. Interconnection Fabrication by EVD	47-54
6.2.2.1. Introduction	47-48
6.2.2.2. State-of-the-Art of Inter-connection EVD	48-54
6.2.3. Subtask 2B. Solid Electrolyte Fabrication	54-59
6.2.3.1. Introduction	54
6.2.3.2. Electrochemical Vapor Deposition (EVD) of Solid Electrolyte	54-56
6.2.3.3. Experiments	56-58
6.2.3.4. Halide Delivery System for EVD of Solid Electrolyte	58-59
6.2.3.5. Status of EVD Fabrication of Solid Electrolyte	59
6.2.4. Subtask 2C. Air and Fuel Electrode Fabrication	60-93
6.2.4.1. Fabrication of the Air Electrode	60-85
6.2.4.1.1 Background	60-61
6.2.4.1.2 Tin Chloride-Indium Chloride Solution Spraying	61-62
6.2.4.1.3 Chemical Vapor Deposition (CVD) of Tin Doped-Indium Oxide Films	62-63
6.2.4.1.4 Results	64-68
6.2.4.1.5 CVD Apparatus Refinement Details	68-70
6.2.4.1.6 Results with Refined Apparatus	71-79
6.2.4.1.7 Film Growth Using Seeding	79-84
6.2.4.1.8 Summary	85
6.2.4.2. Fabrication of the Fuel Electrode	85-93
6.2.4.2.1 Introduction	85

Table of Contents (Continued)

	<u>Page(s)</u>
6.2.4.2.2 Development of a Strong Nickel-Zirconia Fuel Electrode	85-87
6.2.4.2.3 Formation of Fuel Electrode Bands	87-93
6.2.4.2.4 Summary	93
6.2.5. Subtask 2D. Fabrication of the Porous Support Tube	92-118
6.2.5.1. Technical Background	92-95
6.2.5.2. Support Tube Fabrication Experiments	95-114
6.2.5.2.1 Powder Preparation	95-99
6.2.5.2.2 Paste Preparation	99-102
6.2.5.2.3 Forming and Densification	102
6.2.5.2.4 Extrusion and Drying	102-104
6.2.5.2.5 Presintering and Final Firing	104-109
6.2.5.2.6 Results and Discussion	109-114
6.2.5.3. Summary	114-118
6.3 Task 3. Component Testing	119-137
6.3.1. Subtask A. Interconnection Testing	119-125
6.3.1.1. Test Specimen with Lateral Current Flow	119-122
6.3.1.2. Test Specimen with Current Flow Directly through the Film	122-125
6.3.2. Subtask B1. Combination Testing	125-137
6.3.2.1. Early Testing of Interconnection Fuel Electrode Combination Specimens	125-129
6.3.2.2. Recent Combination Testing of EVD-Deposited Interconnection Films	130-136
6.3.2.2.1 Method for Determining Interconnection Film Resistivities in Combination Specimens Having Interfacial Resistance	130-135

Table of Contents (Continued)

	<u>Page(s)</u>
6.3.2.2.2 Experimental Example of Combination Interconnection Film with Interfacial Resistance	135-136
6.3.2.3. Summary	137
6.3.3. Subtask B2. Fuel Cell Stack Fabrication and Testing	138-168
6.3.3.1. Introduction	138
6.3.3.2. Fabrication of Fuel Cell Stack #1	138-143
6.3.3.2.1 Porous Support Tube Characteristics	138-140
6.3.3.2.2 Fuel Electrode Application	140
6.3.3.2.3 Interconnection Application	140
6.3.3.2.4 Electrolyte Application	140-143
6.3.3.2.5 Air Electrode Application	143
6.3.3.3. Alternate Fabrication Sequence	143-153
6.3.3.4. The Structure of Fuel Cell Stack Components	153
6.3.3.5. Fuel Cell Stack Performance	153-166
6.3.3.6. Summary	166-168
6.3.4. Subtask C. Useful Life Testing	168
6.4 Task 4. Alternate Electrolytes and Battery Design	168-170
7.0 Recommendations	171-173
7.1 Air Electrode	171
7.2 Fuel Electrode	171
7.3 Porous Support Tube	172
7.4 Ideal Interconnection Composition	172
7.5 Electrochemical Vapor Deposition (EVD) of the Interconnection	172-173
8.0 Proposed Future Work	174-175

Table of Contents (Continued)

	<u>Page(s)</u>
9.0 References	176-179
10.0 Appendices	180
10.1 Appendix A. Electrochemical Vapor Deposition of Solid Electrolyte	A-1 to A-4
10.2 Appendix B. Analysis of EVD Film	B-1 to B-5
10.2.1 Photoelectron Spectroscopy of Lanthanum Chromites	B-4
10.3 Appendix C. Analytical Techniques for Examina- tion of Thin Oxide Layers	C-1 to C-5
10.3.1 Scanning Electron Microscopy (SEM)	C-1 to C-2
10.3.2 Direct Imaging Mass Analyzer (DIMA)	C-2 to C-4
10.3.3 X-ray Photoelectron Spectroscopy (ESCA or XPS)	C-5
10.3.4 Monochromatic X-ray Powder Diffraction	C-5 to C-6
10.4 Appendix D. Electrical Measurement Apparatus for Component Testing	D-1, D-2
10.4.1 Apparatus Requirements	D-1, D-2
10.5 Appendix E. Crossed-Electrode (CE) Method for Measuring Thin Film Specimen Resistance	E-1 to E-4
10.6 Appendix F. Resistance Measurements on an Interconnection Film-Fuel Electrode Combination Specimen	F-1 to F-5
10.6.1 Two-Contact Method	F-1 to F-3
10.6.2 Three-Contact Method	F-3 to F-5
11.0 Permanent Record Book Entries	G-1
12.0 Acknowledgements	H-1

List of Tables

	<u>Page</u>
6.1 Thermal expansion data of various lanthanum chromites	28
6.2 Summary of RF sputtered $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$ films	41
6.3 Film thickness resistivity and chemical analysis data of as prepared films of air electrode current collector	76
6.4 Process flow sheet of porous support tube fabrication	100
6.5 Fired properties of extruded porous calcia-stabilized zirconia tubes-in-house development	113
6.6 Three point flexure test of porous support tubes	115
B.1 Uniformity of magnesium doping in lanthanum chromite films formed by EVD	B-3

List of Illustrations

	<u>Page</u>
4.1 Schematic cross-Section of a thin film fuel cell	8
4.2 Schematic diagram of a solid oxide electrolyte	9
4.3 Cross-section of the Westinghouse thin film solid electrolyte fuel-cell stack	12
4.4 Schematic of a unit cell design in the thin-film fuel cell	13
4.5 Coal-burning solid electrolyte fuel cell power system	15
6.1 Theoretical dependence of the oxygen deficit, x , in $\text{La}_{1-y}\text{Sr}_y\text{CrO}_{3-x}$ partial pressure at equilibrium	21
6.2 Oxygen loss from $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.15}\text{O}_{3-x}$ versus oxygen partial pressure at 1000°C	23
6.3 Distribution of Mg, La, Cr, Al and Si in $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$	24
6.4 Experimental setup for measuring weight changes of 1000°C if lanthanum chromites in wet air and water/hydrogen mixtures	25
6.5 Oxygen deficit, x , in $\text{La}_{.84}\text{Sr}_{.16}\text{CrO}_{3-x}$ versus oxygen partial pressure	26
6.6 Thermal expansion of lanthanum chromite materials, 25°C to 1000°C to 25°C in air	29
6.7 Powder target sputtering system	32
6.8 RF sputtering powder target	34
6.9 Graphite substrate holder with substrates attached	36
6.10 X-ray powder patterns of $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$	39
6.11 $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$ RF sputtered on a porous nickel cermet fuel electrode at about 300°C	44
6.12 Cross-sections of a lanthanum chromite film over a nickel-zirconia cermet fuel electrode	49
6.13 Reactor arrangement for EVD of Sr-doped LaCrO_3 inter-connection films at temperatures above 1200°C	51
6.14 Arrangement of substrate tube and holder for electro-chemical vapor deposition of electrolyte and inter-connection oxide films	52
6.15 Scheme of oxide film growth by EVD	55
6.16 Determination of electrolyte growth rate in a typical EVD run	57

List of Illustrations (Continued)

	<u>Page</u>
6.17 CVD apparatus: indium oxide-ammonium chloride reactants (using $\text{NH}_3\text{-HCl}$ gases)	63
6.18 Photomicrographs of SnO_2 doped In_2O_3 on zirconia substrate	65
6.19 Resistivity per unit thickness (ρ/δ) versus temperature ($^\circ\text{C}$) for SnO_2 doped In_2O_3	66
6.20 Resistivity versus temperature for In_2O_3	67
6.21 Experimental arrangement for the chemical vapor deposition (CVD) of indium oxide and tin oxide air electrode current collector films	69
6.22 End view (not yet closed) of the alumina chamber of the CVD reactor	70
6.23 Pellets of Reactant oxide sample	70
6.24 Resistivity profile of tin-doped indium oxide films on alumina tubes from three successive CVD experiments	72
6.25 Thermal expansion of a pressed specimen of tin-doped indium oxide, previously heated at 1500°C for 17 hours	73
6.26 Resistivity profile of CVD tin-doped indium oxide films on ceramic target tubes	75
6.27 Micrographs showing the type of films obtained from CVD experiments $\text{IN}_{II} = 1$ (a) and $\text{IN}_{II} - 4$ (b)	77
6.28 Resistivity versus temperature behavior of tin-doped indium oxide film deposited on bentonite-doped calcia-stabilized zirconia	80
6.29 Resistivity versus temperature behavior of tin-doped indium oxide film deposited on calcia-stabilized zirconia tube	81
6.30 Resistance profile of tin-doped indium oxide film across seeded and non-seeded sections of calcia-stabilized zirconia tube	82
6.31 Porosity of tin-doped indium oxide film caused by unknown variables during chemical vapor deposition	84
6.32 Arrangement for nickel plating of fuel electrodes	88
6.33 Fuel Electrode resistance changes with temperature and reduction of resistance by electroplating	89
6.34 Etching method for nickel cermet electrode	91
6.35 Apparatus for fuel electrode etching	92

List of Illustrations (Continued)

	<u>Page</u>
6.36 Extrudes Assembly	96
6.37 Iler rotating disk crusher	97
6.38 Trost pulverizing mill	97
6.39 Syntron vibrating sieve shaker	98
6.40 Baker-Perkins kneading machine	101
6.41 Extrusion die set up with 500 g capacity of material	103
6.42 Extrusion die set up for 1000 g of capacity of material	103
6.43 Extruder parts, showing different spider core pin assemblies	105
6.44 Extruder parts modified to handle a large material batch per extrusion	105
6.45 Samples after bisque firing in the Harrop kiln	106
6.46 Overall view of bisque fired samples in the Harrop kiln	106
6.47 Early method used to hang-fire tubing in the Harrop kiln for bisque firing	106
6.48 Extruded tubing after bisque firing	107
6.49 Bisque fired tubing cut into 6 inch lengths prior to final firing	107
6.50 Overall view of gas pot furnace during firing of support tubes	108
6.51 Close up of gas pot furnace during final firing of support tubes	108
6.52 Close up of gas pot furnace showing refractory cover with optical pyrometer sight holes	110
6.53 Sample configuration and arrangement during final firing of support tubes	110
6.54 View showing method of loading and unloading samples into pot furnace	111
6.55 Furnace crucible arrangement without the sample holder	111
6.56 Samples after firing in high temperature gas furnace	112
6.57 Thermal expansion of porous calcia-stabilized zirconia-tube-Sample B-11	116
6.58 Interior surface of extruded calcia-stabilized zirconia tubes In House development	117

List of Illustrations (Continued)

	<u>Page</u>
6.59 Exterior surface of extruded calcia-stabilized zirconia tubes-In House development	118
6.60 Schematic of apparatus for measuring the electrical characteristics of combination specimens	120
6.61 Specimen geometry for thin film interconnection resistivity measurement	121
6.62 Electrical resistivity of $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$	123
6.63 Schematic of crossed-rod method for measuring electrical contact resistance	124
6.64 Schematic of crossed-electrode geometry for combination testing	124
6.65 Effective specimen resistance vs temperature for a crossed-electrode specimen of $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$	126
6.66 Method of attaching measurement contacts to tubular specimens	127
6.67 Resistivity vs temperature for a tubular combination specimen	129
6.68 Cross-sectional view of ideal combination specimen, consisting of fuel electrodes, interconnection film and platinum electrodes for resistance measurements	131
6.69 Cross-sectional view of combination specimen having an interfacial resistance layer at the fuel electrode-interconnection film boundary	131
6.70 Equivalent resistance network for combination specimens	132
6.71 Resistivity(hydrogen-water atmosphere) versus temperature for one of the first successfully-doped EVD-deposited interconnection films	136
6.72 Cross section of two interconnected fuel cells	139
6.73 Fuel electrode over porous support tube (top) and interconnection over entire fuel electrode (bottom)	141
6.74 Interconnections over fuel electrodes, separated by inter-cell gaps	142
6.75 EVD electrolyte applied over entire stack structure	144
6.76 Electrode removed over interconnection: by sandblasting	145
6.77 Oxide tape masking before CVD application of doped indium oxide	146

List of Illustrations (Continued)

	<u>Page</u>
6.78 Stack after indium oxide CVD and demasking	147
6.79 Fuel electrode bands produced by bipolar electro-chemical etching (top) Application of spheroidized zirconia tape and interconnection area masking (bottom)	148
6.80 EVD electrolyte applied over entire stack structure	149
6.81 Electrolyte masking tapes removed, showing exposed fuel electrode before EVD of interconnection materials	150
6.82 Masking of active cell area before EVD of Interconnection material	151
6.83 EVD-lanthanum chromite layer over total stack (top) Demasked active cell areas and ready for indium oxide CVD (bottom)	152
6.84 Porous electrolyte skeleton as part of the composite air electrode	154
6.85 Fault-free electrolyte overlap of interconnection band	155
6.86 Good-electrolyte-interconnection overlap at inter-cell gap (top) Good electrolyte-interconnection overlap at cell side (bottom)	156
6.87 Cross-section through active cell area of a completed stack (top) Cross-section through interconnection of a completed stack (bottom)	157
6.88 Dense electrolyte overlap over lanthanum chromite inter-connection (top) Dense lanthanum chromite overlap over electrolyte (bottom)	158
6.89 Interface of fuel electrode and interconnection showing interface layer	159
6.90 Test arrangement for thin film solid oxide fuel cell stack	160
6.91 Performance of 5 cell stack	162
6.92 Performance of individual cells of five cell stack	163
6.93 Voltage loss of five cell stack due to ohmic resistance	164
6.94 IR voltage loss of individual cells between 300 to 600 hours of continuous operation	165
6.95 Performance of a three-cell stack, as part of a five cell arrangement	167

List of Illustrations (Continued)

		<u>Page</u>
6.96	Interconnection appearance after 113 h of operation and two complete temperature cycles	169
A.1	Scheme of oxide growth by EVD	A-2
B.1	Lanthanum chromite EVD film in a porous nickel electrode	B-2
C11	Scanning electron microscopy (SEM)	C-3
C.2	CAMECA SMI-300 instrument	C-4
C.3	ESCA equipment	C-6
E.1	Schematic of crossed-rod method for measuring electrical contact resistance	E-2
E.2	Schematic of crossed-electrode geometry for combination testing	E-2
E.3	Correction for the apparent specimen resistance when it becomes comparable to the lateral electrode resistance in a crossed electrode measurement	E-4
F.1	Enlarged cross-section showing various specimen layers and measurement contacts	F-2
F.2	Distributed resistance analog of the specimen films and contacts	F-2

1.0 ABSTRACT

The two year program has been completed with the following noteworthy accomplishments.

1. A rare-earth chromite, in particular, $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$ was identified, synthesized by RF-sputtering tested for resistivity, thermal expansion and inertness in contact with yttria-stabilized zirconia, and was found promising as a candidate interconnection material.
2. Films of these interconnection materials have been successfully deposited onto stabilized zirconia tubes by electrochemical vapor deposition (EVD) and the technique has been used to fabricate such films in building fuel cell stacks.
3. Tin-doped indium oxide and antimony-doped tin oxide air electrode current collector materials have been successfully (CVD) chemically vapor deposited, as thin films, onto zirconia tubes.
4. Fabrication procedures for the preparation of thin films of the nickel-cermet fuel electrode and yttria-stabilized zirconia solid electrolyte have been re-verified and improved for use in preparing unit cells and cell stacks on the program.
5. An in-house extrusion technology for porous calcia-stabilized zirconia tubes has been developed and has been used to provide suitable support tubes for component combination samples, unit cell and cell stack sample preparation.
6. Test concepts for component combinations and for unit cells and cell stacks have been evolved, particularly, the crossed electrode technique, and test equipment has been designed, built and used to evaluate fuel cell components and their interfaces.

7. A five-cell fuel cell stack has been fabricated and operated for 700 hours at 200 mA/cm^2 at $950\text{-}980^\circ\text{C}$ and was subjected to three temperature cycles during the testing. Three series connected cells of this five cell stack met the 80% voltage efficiency final target objective of the program (less than 10% voltage degradation in 700 hours - with only 300 hours required).
8. All essential program objectives have been attained.

2.0 PROGRAM SUMMARY

Highlights of progress on the program during the two years are presented for the various task and subtasks, as specified in detail in the Design Plan of the program. ⁽¹⁾

TASK 1. Materials Identification and Selection.

Subtasks A and B. Interconnection Search and Identification

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

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

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

Subtask C. Development of Other Stack Components

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

- support tube -- porous, calcia-stabilized zirconia (15 mol % calcia)
- fuel electrode -- nickel cermet (nickel deposited on a porous, stabilized zirconia skeleton)

- solid electrolyte -- yttria-stabilized zirconia (from 8 mole % to 12 mole % yttria)
- composite oxide air electrode -- tin-doped indium oxide (1 to 5 wt % SnO_2) current collector, with praeosodymium oxide impregnation of the zirconia skeleton

TASK 2. Fabrication Techniques

Techniques for producing films of the various active components proceeded to the level where they are being used to produce fuel cells and fuel cell stacks. An extrusion process has been developed to produce, in-house, the porous support tubes.

Subtask A. Interconnection

RF sputtering has been used to produce films for basic property evaluations, whereas an electrochemical vapor deposition (EVD) technique has been developed that can produce modified rare earth chromite compositions that are both leak-tight and conducting, as thin films ($\sim 40 \mu\text{m}$).

Subtask B. Electrolyte

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

Subtask C. Air and Fuel Electrode

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

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

Subtask D. Porous Support Tube

Extrudable mixtures, prepared by combining selective size fractions of refractory starting powders and calcining at 1780°C, produced tubes that met the specifications of open porosity (>25 volume percent), tensile strength (>5000 psi) and thermal expansion ($\sim 10 \times 10^{-6}$ mm/°C at 1000°C). Surface pores of the tubes were 10-11 μ m in diameter with some variation in pore sizes caused by agglomerates of water swelling starch plasticizers used in the batch material preparation for extrusion.

TASK 3. Component Testing

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

Subtask A. Interconnection

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

Subtask B. Combinations

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

Subtask C. Useful Life Testing

A 5 cell fuel cell stack was fabricated and evaluated on the program. Three series connected cells of this stack met the program goals -- displaying 80% voltage efficiency at 200 mA/cm² for 700 hours with less than 10% voltage degradation at 950-980°C in a hydrogen - 3% water vapor fuel atmosphere.

TASK 4. Alternate Electrolytes and Battery Designs

Work scheduled in this area involved:

- 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 indicated problems, particularly, with respect to mechanical over-stressing of cell or cell stack component(s).

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

Preface

For purposes of providing background information, to those readers who may be unfamiliar with the operation, design concept, and application principle of the high temperature, solid electrolyte fuel cell, Sections 3.0, 4.0, 4.1, 4.2 and 4.3 have been included in the Final Report.

3.0 INTRODUCTION

Fuel cells are electrochemical generators of direct current electricity. Unlike conventional generators, based on heat cycles, they have no Carnot efficiency limitations, and can, theoretically, yield high energy efficiency. Of all fuel-cell power systems, that based on a stabilized-zirconia, solid electrolyte offers the highest achievable efficiency. A battery design study, conducted prior to this program, indicated that power densities of 23 Kw/ft^2 of fuel cell module are achievable with the then state-of-the-art materials and fabrication processes when the stacks are operated at 80% electrical efficiency.⁽²⁾ The high-temperature solid-electrolyte fuel cell operates at 1000°C , without the need of expensive catalysts, on a carbon monoxide-hydrogen gas mixture, provided by the gasification of coal. The fuel cell generator operates at 1000°C for several reasons: a) the resistivity of the solid electrolyte is sufficiently-low to permit high levels of electrical efficiency at high current densities and b) the heat released in the fuel oxidation can be efficiently transferred to the endothermic coal gasification reaction. Also, since coal is the basic fuel, if an economically competitive power plant, based on this fuel-cell type, can be developed, it will contribute to natural-resource conservation.

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

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

- The heat rejected by the fuel cell is employed to gasify coal, thus minimizing waste heat and avoiding thermal pollution of the environment.
- The fuel cell generating process does not require cooling water, consequently, siting of plants will not be dependent on plentiful water supplies.

The commercial feasibility of this new power system greatly depends on the useful life of the generator. At the onset of this program, the useful life of the thin-film battery had not achieved 100 hours. The ERDA-directed, NASA-managed Energy Conversion Alternatives Study, conducted in 1975-76 at the Westinghouse Research Laboratories⁽³⁾, indicated that, for fuel-cell power systems to be competitive from an electricity-cost standpoint, the useful life of the fuel cell module must exceed 30,000 hours.

4.0 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:

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

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

In this section a coal-burning fuel cell power system is described, including: (1) how solid-electrolyte cells produce electrical energy, (2) how individual cells can be combined to form high-performance batteries, and (3) how batteries can be combined with auxiliary equipment into a power plant concept. Also reviewed are the major technical problems that must be resolved to allow demonstration of a long-lived, high-performance fuel-cell battery.

4.1 HOW SOLID ELECTROLYTE FUEL CELLS GENERATE ELECTRICITY

As shown in Figure 4.1, a solid electrolyte fuel cell consists of four basic components: an air electrode, a solid electrolyte, a fuel electrode, and a porous insulating tube. A fifth component, the interconnection between adjacent cells, is not shown.

The porous tube of stabilized zirconia, which serves as a mechanical support for the fuel cell, has an approximate wall thickness of 1000 μm . In contrast, the individual component layers lie in the thickness range of 20 to 50 μm .

Figure 4.1 - Schematic cross-section of a thin-film fuel cell.

Exposed to the air flow is the air electrode. It is an electronically conductive oxide, such as $(\text{In}_2\text{O}_3)_{0.98}(\text{SnO}_2)_{0.02}$, fabricated in a porous structure that is readily permeated by oxygen from air which flows over it. Praesodymium oxide is discontinuously deposited onto this porous electronic conductor surface. This active PrO_2 effects the necessary $\text{O}_2(\text{g})$ to $2\text{O}^=$ transition. Oxygen molecules from the air accept electrons at active PrO_2 sites, leaving the electrode positively charged, and forming oxygen ions, $\text{O}^=$, as shown in Figure 4.2. Each O_2 molecule removes four electrons and forms two $\text{O}^=$ ions, as the cell operates.

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

Figure 4.2 - Schematic diagram of a solid electrolyte fuel cell, indicating how oxidation of the fuel generates electric current to the external load.

O^{2-} ions can enter the second component of the cell, a dense zirconia ceramic, such as yttria-stabilized zirconia. This is the solid electrolyte of the cell. At the operating temperature of $1000^{\circ}C$, oxygen ions pass through this layer, due to the oxygen concentration gradient across the ceramic. (If an O^{2-} enters at the air electrode-electrolyte surface, an O^{2-} emerges at the electrolyte-fuel electrode surface, thus preserving the electrical neutrality of the material). The gases on either side of the cell will not penetrate through this impervious electrolyte layer so that the reaction can only take place when current is drawn from the battery. Since the ceramic electrolyte will not conduct electrons, no short circuit can occur in the cell.

Exposed to the fuel flow in the figure is the fuel electrode. The porous fuel electrode is a nickel-zirconia cermet. At the fuel electrode the fuel gases, H_2 and CO , react with the emerging O^{2-} ions to form reaction products, H_2O and CO_2 . Electrons emerge from the fuel electrode, In this way the fuel electrode becomes negatively charged.

These three layers -- an electrolyte sandwiched between two electrodes -- constitute a single solid-electrolyte fuel cell. The voltage developed between the electrodes of the cell is a function of the oxygen partial pressure in the fuel gas. When current is drawn, the cell voltage lies, typically, between 0.95 and 0.65 volt.

Electrical energy and power is delivered by the cell when a load is connected between the two electrodes. Electrons will then flow from the negative fuel electrode to the positive air electrode through the load circuit. Current can be drawn from a cell, as long as air and fuel gases are supplied and the combustion products removed. Current densities of nearly 300 mA/cm^2 can be obtained from solid-electrolyte cells, while still maintaining cell efficiency at 80%. The output voltage produced at such currents is a function of the ohmic losses and concentration polarization losses in the electrodes.

4.2 FABRICATION OF FUEL-CELL STACKS

To obtain the voltages required for a practical system, cells must be connected in series. The technique, illustrated in Figure 4.3, provides a potentially low-cost method of making a series-connected stack of cells. This modular stack design is aimed at minimizing ohmic losses at relatively high current densities^(4,5). It is necessary to provide an electrolyte surface area of approximately $5 \text{ ft}^2/\text{Kw}$, based upon state-of-the-art single cell performance.

CROSS SECTION THROUGH THE WALL OF A THIN-FILM FUEL-CELL STACK

Figure 4.3 - Cross-section of the Westinghouse thin-film solid electrolyte fuel-cell stack.

A group of cells, each about 0.5 cm wide around a porous tube of about 1.3 cm O.D., are series-connected to form a stack. As schematically shown in the cross-section of Figure 4.3, all cells on the tube are series-connected by joining the air electrode of one cell to the fuel electrode of an adjoining cell, through an electronically conducting interconnection. The interconnection must be fabricated as a gas-tight film, just as in the case of the electrolyte. Particular attention must be paid to the junction between the electrolyte and interconnection films to ensure gas impermeability.

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

A design study at Westinghouse⁽²⁾ indicated that, in order to maximize the power generated per unit length of battery, the unit cell length must be approximately 0.5 cm. Figure 4.4 shows that the unit cell length is the sum of four characteristic lengths: l_c , the active cell length; l_i , the active interconnection length; and, l_a and l_f , the gap lengths between adjacent air electrodes and fuel electrodes, respectively.

Figure 4.4 - Schematic of a unit cell design in the thin-film fuel cell.

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

4.3 HIGH TEMPERATURE, COAL-BURNING FUEL CELL SYSTEM

A coal-burning, solid-electrolyte fuel cell system will include a coal gasifier, gas cleaning and circulating equipment, a fuel cell generator, a heat exchanger and a DC to AC inverter. Coal or coal char is fed to the coal gasifier, along with a portion of the hot CO_2 and H_2O combustion products and waste heat from the fuel cell generator (Figure 4.5). Here, coal reacts with the combustion products to form CO and H_2 fuel gases. The gases are fed to the fuel cell generator, after treatment to remove particulate material and sulfur compounds. In the generator, the fuel gases are electrochemically oxidized to CO_2 and H_2O .

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

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

The air necessary for the operation of the generator is brought in separately. The N_2 of the air and the unreacted O_2 emerge from the generator, exchange heat with the incoming air, and exhaust to the surroundings. Suitable AC power is available to tie-into a utility grid network.

Fig. 4.5. Coal burning solid-electrolyte fuel cell power system.

5.0 THE PRESENT PROGRAM

The purpose of the two-year, DOE-sponsored research program under Contract No. EY-C-76-03-1197, was the demonstration of the technical feasibility of a high-temperature, solid-electrolyte fuel cell, building on the technological base just described. The bulk of the work consisted of identifying and selecting candidate materials and their fabrication, 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 was on the invention and fabrication of an interconnection film, which has the following properties at 1000°C, the proposed temperature of stack operation:

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

Emphasis was placed on the fabrication of porous support tubes of calcia-stabilized zirconia to the desired specifications of tensile strength, porosity, surface finish, and purity. Tubes were to be prepared in house and evaluated for compliance with the following specifications:

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

The culmination of all efforts on the program was the fabrication and testing of a stack, consisting of a minimum of three cells. Test data were obtained from operating this stack under simulated operating conditions.

6.0 OVERALL TECHNICAL EFFORT

6.1 TASK 1: MATERIALS IDENTIFICATION AND SELECTION

The overall purpose of this task was 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.

6.1.1 Subtask 1A. Interconnection Literature Search

The individual cells of the thin layer, zirconia electrolyte, fuel cell battery are connected in series by a film of electronically conducting oxide. Earlier work had indicated that manganese-doped cobalt chromite⁽⁶⁾ and chromium sesquioxide⁽⁷⁾ have sufficient electronic conductivity, as well as stability, toward the oxidizing and reducing atmospheres encountered in a working fuel cell to be possibilities as interconnections in this application. However, these materials have a serious coefficient of expansion mismatch with other components of the cell. This mismatch was thought to be responsible for interconnection cracking problems which occurred in previous versions of this type of fuel cell, which used a chromium sesquioxide interconnection.

As a consequence, we directed a literature search with a view to obtaining new candidate interconnection materials with more suitable thermal expansion properties. Modification of available materials, by doping or layering with a second material, was considered as an alternative, if a superior material could not be found.

Guidelines for selection of new candidate interconnection materials were as follows: (1) moderate cost, (2) stability in air and the fuel gas, (3) resistivity in the working environment of 50 ohm-cm, or less, and nearly 100% electronic conductivity, (4) non-reactivity with other cell components, (5) thermal expansion characteristics compatible with other cell components, (6) low volatility of components of the oxide, (7) absence of destructive phase transformations between room temperature and 1000°C, (8) fabricability as a thin, gas impervious layer. It

was expected that a material with all these combined properties should have a good probability of remaining a useful interconnection for at least 30,000 hours of continuous fuel cell operation.

The result of this search was that no material or compound with only one metal ion as the major component was found to satisfy all requirements. However, five systems of multi-element compounds were selected for further study, with the intent that they be modified, by appropriate doping and substitution of other cations for all or part of the major metal ion components, to give the desired properties. The systems selected for further investigation were the following:

1. rare earth chromite system
2. alkaline or rare earth titanate systems
3. alkaline earth chromite system
4. cerium oxide with additions of niobium or tantalum and other oxides
5. rare earth nickel-cobalt-manganese oxide systems

The rare earth chromite system, lanthanum chromite in particular, was subsequently chosen for intensive investigation as an interconnection material.

6.1.2 Subtask 1B. Modification of Interconnection Materials

An initial experimental survey was made to test lanthanum chromite and other interconnection material candidates for any obvious interactions with other cell components. Further work on the selected systems investigated thermal expansion and electrical conductivity, along with the effects on these properties of additions, or substitutions, of small amounts of other metal ions for the major constituents of the oxides.

From these studies, the leading interconnection candidate that emerged was lanthanum chromite, doped with (1) magnesium, or other alkaline earth ions, to obtain sufficient electrical conductivity, and (2) aluminum ions, to adjust thermal expansion properties. Work on similar lanthanum chromite materials by others in the MHD area also

indicated excellent high temperature stability of these materials. Subsequently, long term stability of lanthanum chromite in fuel cell environments was reported by Rohr⁽⁸⁾ at the ERDA-sponsored Solid Oxide Fuel Cell Workshop at Brookhaven National Labs in May 1977. This further strengthened the basis for selection of lanthanum chromite as the interconnection material.

Ensuing work on lanthanum chromite properties then entailed studies of (1) changes in oxygen content of lanthanum chromite as a function of the type and amount of magnesium, strontium, and aluminum additives; (2) the preparation technique on the composition, adherence, and integrity of the films formed by electrochemical vapor deposition or radio-frequency sputtering processes; and (3) thermal expansion of lanthanum chromite with different additions of magnesium, strontium, barium, aluminum, cobalt, and nickel oxides.

6.1.2.1 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} atmospheres of oxygen at the fuel electrode. Under the fuel-rich condition, lanthanum chromite with an alkaline earth substituent loses a small amount of oxygen from the crystal lattice. We now consider possible mechanisms for this loss.

Oxygen loss from these materials may be considered to result, most probably, from the following type of gas-solid oxide reaction

(written here for the case of $\text{LaCr}_{.75}\text{Al}_{.23}\text{Mg}_{.02}\text{O}_{3-x}$)

or, written only in terms of the reacting solid state ions in the crystal lattice and gaseous oxygen species

where Cr^{4+} may also be considered as a positive hole associated loosely with a Cr^{3+} ion, O^- is an oxygen ion, and $\square^0$ is a vacancy at a normal oxygen ion site in the perovskite crystal structure. We may write an equilibrium constant K for this reaction as follows:

$$K = \frac{(\text{Cr}^{3+})^2 (\square^0) (\text{O}_2)^{1/2}}{(\text{Cr}^{4+})^2 (\text{O}^-)} \quad (1)$$

where the terms in parentheses are thermodynamic activities of the various ionic species, and where (O_2) can be considered to be approximately the same as P_{O_2} , the pressure of oxygen under the reacting conditions of the fuel cell. For purposes of plotting a graph, we write in the logarithmic form and rearrange Eq. 1 to give

$$\log K^2 P_{\text{O}_2} = 2 \log \frac{(\text{Cr}^{4+})^2 (\text{O}^-)}{(\text{Cr}^{3+})^2 (\square^0)} \quad (2)$$

Figure 6.1 is a calculated plot which illustrates the pressure dependence of $\square^0$ on $\log K^2 P_{\text{O}_2}$ to be expected if it is as predicted by Eq. 2. It is plotted for three values of y in $\text{La}_{1-y}\text{Sr}_y\text{CrO}_{3-x}$.

Experimentally, this type of S shaped curve typifies the general dependence of the oxygen content of magnesium-doped lanthanum chromite, where Mg^{2+} is present on about 2% of small B sites or, possibly, the larger A sites of the ABO_3 perovskite structure. Much larger alkaline earth concentrations, as with $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_{3-x}$, exhibited higher oxygen dissociation pressures and deviated considerably from the Eq. 2 relationship. In all cases, the maximum amount of oxygen that could be removed experimentally at very low oxygen partial pressures (e.g., less than 10^{-20} atm) corresponded to less than one molecule of O_2 for each four ions of Mg^{2+} or Sr^{2+} in the crystal lattice of lanthanum chromite.

Figure 6.2 shows the application of Eq. 2 to determine the amount of magnesium actually in solid solution in a lanthanum chromite preparation of nominal composition $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$. In this

Fig. 6.1 —Theoretical dependence of the oxygen deficit x in $\text{La}_{1-y}\text{Sr}_y\text{CrO}_{3-x}$ on oxygen partial pressure at equilibrium

instance, the DIMA (Direct Imaging Mass Spectrometer) suggests the presence of a second phase, or phases, containing a considerable portion of the total magnesium combined with silica, chromium, and aluminum components (Figure 6.3A). In Figure 6.2, experimental data using the high temperature microweighing apparatus (shown schematically in Figure 6.4) are compared with a calculated curve based on Eq. 2. For the calculation, the amount of magnesium in solid solution and K , the equilibrium constant, were adjusted to most nearly coincide with the experimental data. Calculation based on a nominal composition of the major lanthanum chromite phase of $\text{La}_{.975}\text{Mg}_{.025}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_{3-x}$ with a value for the equilibrium constant K in Eq. 1 of $10^{-6.3}$ fits the data with only a moderate deviation, as shown by Figure 6.2. It should be noted that the magnesium may actually lie on chromium rather than lanthanum sites, but such a change makes a negligible difference in the shape of the calculated curve, so that only the degree of doping and not the location of the magnesium can be determined by this method. Various association equilibria may also occur in this system, but their main effect is to change the position of the curve with respect to the oxygen pressure axis ($\log P_{\text{O}_2}$), rather than producing any appreciable change in curve shape.

The effect of increasing the temperature of the alkaline earth doped lanthanum chromites is to increase the oxygen loss at a given oxygen partial pressure. This is illustrated in Figure 6.5 for the case of $\text{La}_{.84}\text{Sr}_{.16}\text{CrO}_{3-x}$. For example, increasing the temperature from 800° to 1000°C increases the oxygen loss from this oxide more than a factor of ten at 10^{-16} atm O_2 . These data were all taken using samples of about 70% porosity. This open porosity allows rapid penetration of oxygen into the internal pores for more rapid equilibration.

6.1.2.2 Thermal Expansion Studies

The goal of these studies was to obtain additional information on the type and quantity of additives to lanthanum chromite which are necessary to eliminate the orthorhombic-to-rhombohedral phase transformation and to adjust thermal expansion to about 10×10^{-6} mm/ $^\circ\text{C}$, a value intermediate to that of the zirconia electrolyte and the indium oxide air electrode. Compositions in which 25% of the Cr^{3+} is replaced by Al^{3+} ,

Fig. 6.2 - Oxygen loss from $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_{3-x}$
 vs. oxygen partial pressure at 1000°C

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 6.3 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.

Fig.6.4— Experimental setup for measuring weight changes of lanthanum chromites in wet air and water/ hydrogen mixtures.

Curve 693338-A

Fig. 6.5 — Oxygen deficit x of $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_{3-x}$ vs oxygen partial pressure

or 8% of the La^{3+} is replaced by Ba^{2+} , are examples which fulfill the thermal expansion criteria. It now appears, however, that doping by any alkaline earth should be kept well below 2%, to reduce oxygen loss from the lanthanum chromite in fuel atmospheres, which, in turn, would enhance the electrochemical oxygen leakage through the interconnection. This leaves as the best interconnection candidate, lanthanum chromite with about 25% of the Cr^{3+} (i.e., the B sites in the ABO_3 perovskite structure) replaced by Al^{3+} and less than 2% of either the La^{3+} or Cr^{3+} sites filled by alkaline earth ions (Mg^{2+} , Sr^{2+} , Ba^{2+}). At this stage, Mg^{2+} is the preferred alkaline earth substituent from the standpoint of ease of incorporation in the EVD (electrochemical vapor deposition) process. Table 6.1 lists thermal expansion data for several of the lanthanum chromite compositions studied. Figure 6.6 shows a graphical comparison of the thermal expansion curves of lanthanum chromites with $\text{Al}_{.25}$, $\text{Sr}_{.16}$, and $\text{Mg}_{.05}$ contents. It is seen that the additions of either the strontium or aluminum component eliminates the phase transformation.

6.1.2.3 Radio Frequency (RF) Sputtering of Interconnection Material.

RF sputtering was used as a means of producing interconnection films of desired composition.

6.1.2.3.1 Background.

At the start of this project, the major problem was to find a material which would meet the requirements of the fuel cell interconnection material. It was anticipated that a number of different compounds would have to be evaluated and the composition adjusted until the proper ratio of components was found. It would be necessary to have a means of depositing these various compounds in thin film form, with some assurance that the films had the right composition, especially as to the proper ratio of the cation elements.

Due to its versatility, RF sputtering was selected as the best fabrication technique to evaluate a variety of mixed oxides of various

TABLE 6.1

THERMAL EXPANSION DATA OF VARIOUS LANTHANUM CHROMITES

Compound	Phase Transformation °C	Thermal Expansion Between 25-1000°C m/m/°C
$\text{La}_{.95}\text{Mg}_{.05}\text{CrO}_3$	~270	8.4×10^{-6}
$\text{LaCr}_{.85}\text{Mg}_{.15}\text{O}_3$	~310-330	9.3×10^{-6}
$\text{La}_{.84}\text{Sr}_{.16}\text{CrO}_3$		10.9×10^{-6}
$\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$		9.9×10^{-6}
$\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.5}\text{Al}_{.5}\text{O}_3$		11.0×10^{-6}
$\text{La}_{.84}\text{Sr}_{.16}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$		10.0×10^{-6}
$\text{LaCr}_{.8}\text{Co}_{.2}\text{O}_3$	~130-150	11.5×10^{-6}
$\text{LaCr}_{.8}\text{Ni}_{.2}\text{O}_3$	~330-365	9.2×10^{-6}
$\text{La}_{.92}\text{Ba}_{.08}\text{CrO}_3$		10.3×10^{-6}

Fig. 6.6. Thermal Expansion of Lanthanum Chromite Materials, 25°C to 1000°C to 25°C in Air

compositions. RF sputtering has a number of advantages as a method of deposition of thin films. One of its most attractive features for this work is the capability of depositing multi-component films, keeping the chemical composition of the films approximately the same as that of the target material. This is due to the fact that when sputtering from a multi-component target, an equilibrium point is rapidly reached where the surface of the target is sufficiently deficient in the material with the higher sputtering rate to just compensate for its higher rate. Thus, after a few minutes of sputtering from a fresh target, the composition of sputtered material will equal that of the target.

This does not mean that the deposited films will have the same composition as the target, especially for the more volatile components. If the sticking coefficients (the fraction of the impinging atoms which adhere to the substrate) vary between elements, then the composition of the film will be deficient in those components having a low sticking coefficient. In particular, the films would be expected to be oxygen deficient, as formed. In addition, when deposited onto an unheated substrate, the film tends to develop an amorphous structure. Therefore plans were made to carry out a post-deposition anneal, which would crystallize the films. This would be done in an oxygen atmosphere to compensate for the as-deposited non-stoichiometry.

Another major advantage of sputtering as a method of depositing films is the capability of changing targets readily. Once the deposition process has been optimized for a particular oxide, minor changes in this oxide, especially in terms of the cation, would not change the deposition parameters significantly.

Most sputtering targets are usually fabricated using a hot-pressed material which is bonded to the sputtering head. A large amount of material is required and the actual hot pressing, which is done under vacuum, is time consuming. To simplify this, a decision was made to use a powder target in the initial experiments. In this case, an upward sputtering system was needed where the material was merely poured, or settled, onto a plate which was then mounted to the target assembly.

After using the powder target techniques to arrive at an optimum composition for the interconnection material, more permanent hot-pressed target structures were fabricated. These were then used to produce uniform interconnection test structures.

6.1.2.3.2 Technical Approach.

An upward sputtering system with a powder target assembly, designed and made in-house, is shown in Figure 6.7. This equipment takes a 4" diameter target. The target assembly has a copper head which is water cooled. An aluminum plate is attached to the head with a threaded stud. The system has a 500 watt power supply and the matching circuit is custom designed. The unit operates in a standard diode arrangement.

Initially the aluminum backing plate was simply a flat plate to hold the powdered target material. The powder (such as $\text{La}_{.95}\text{Mg}_{.05}\text{CrO}_3$) was settled onto the plate from a slurry, followed by a bakeout to eliminate moisture. This powder was only slightly caked and proved quite difficult to handle. The first improvement made was a slight lip, machined into the backing plate, to retain the material. The ground shield is brought over this lip to prevent any sputtering from this edge.

A number of problems occurred with the use of this powdered target approach. The initial problem associated with the handling was overcome by the use of the machined lip on the backing plate. However, it was found that the target continued to degrade severely after a few runs. This degradation was in the form of large areas of aluminum backing plate being exposed, requiring a new target to be fabricated after every other run. The exposed aluminum would be sputtered and incorporated into the deposited film. Aluminum was chosen as a backing material since its effect on the deposited film should be small; however, the exposure of large areas precluded any run-to-run reproducibility. This problem was traced to an apparent instability during the initial startup of the discharge. This target assembly was slightly unstable until the gas

Fig. 6.7 - Powder target sputtering system

pressure and matching network could be properly adjusted. This instability produced a number of "hot spots" in the face of the target, spots where the plasma was very intense. The hot spots would erupt, either from heating of trapped gas in the powder, or possibly from vaporization of the target material itself, since the localized power density can be very high. Each of these eruptions would expose a small area of the backing plate. After a number of such events, a significant fraction of the backing plate would be exposed.

The exact cause of this problem was not known. The sputtering head and ground connections were redesigned and some changes made in the matching network of the RF sputtering supply. These eliminated the problem associated with the instability. In addition, tighter controls on the initial pump down, to avoid turbulence, and decreased vibrations eliminated some of the other problems associated with the powder target.

A number of runs were made with the original design of the RF sputtering system. The depositions were made from a powdered $\text{La}_{.95}\text{Mg}_{.05}\text{CrO}_3$ target onto an unheated substrate. This target is shown in Figure 6.8. Using a 4" diameter target and a power input of 300 watts (3.7 watts/cm^2), deposition rates of approximately $80\text{\AA}/\text{minute}$ were obtained. This rate was obtained using argon as the sputtering gas. The addition of oxygen, which would be required to control stoichiometry in the deposited film, would be expected to lower this rate somewhat. Initial layers were between 7 and 10 microns in thickness. Later depositions, with run times as long as 85 hours, gave thicknesses of over 40 microns. These films adhered well to the substrate.

All these runs were made with an unheated substrate. However, since there is a considerable amount of heat involved in the sputtering process, the substrate temperature rose during the deposition, reaching approximately 150°C at the end of the longer runs.

The films, as deposited, appeared dense. However, after an air treatment at 1000°C , they exhibited some cracking, usually in the form of hairline cracks which penetrated to the substrate. No measurements were made on the amount of leakage such cracks would produce, but the aim of the process is to obtain a film impervious to gas flow and these were therefore considered unacceptable.

Figure 6.8. Powdered RF sputtering target.

These cracks might be occurring either because of a recrystallization during the oxygen treatment or from stresses produced by the film being deposited onto a cold substrate which are relieved during the anneal. Therefore, it was reasoned that a higher substrate temperature should not only produce a denser film due to the higher surface diffusion of the incident atoms, resulting in better ordering of the deposited film, but should be somewhat crystallized during the deposition and be less stressed after growth. Additionally, if the film was deposited at an elevated temperature (500°C), the thermal expansion mismatch between the film and support tube would be less severe, since the temperature differential would be, essentially, reduced one half.

With this in mind, a substrate heater was designed and installed in the vacuum system. The various electrical connections are sufficiently shielded so they are not affected by the plasma. It was expected that this would not only improve the film properties but also the run-to-run uniformity.

The substrate holder had initially been machined from aluminum which would be limited to operation below 660°C. This was replaced with one machined from graphite, which is shown in Figure 6.9. Substrate heating is effected with two 500 watt cartridge heaters. The samples are mounted onto the graphite block by screws. On the more recent runs, an indium was used as a thermal conductor between the substrate and the substrate holder. This unit has been tested to over 800°C. The major problem with temperatures higher than about 400°C, was the temperature rise of the top plate and bell jar during the deposition. This was produced from radiation from the substrate, together with the heat losses resulting from the high power used for the sputtering. These factors, coupled with long run times, lasting up to 80 hours, raised the temperature of the vacuum system to levels which were unsafe for the equipment components.

Normal heat baffles were of little use, since the long run times would raise the temperature of the baffle near that of the substrate. Therefore, a water-cooled baffle was designed and installed. The baffle is a stainless steel shield surrounding the substrate and target assembly.

Figure 6.9. Graphite substrate holder with substrate attached.

Copper coils were brazed to the baffle and connected to stainless steel flexible tubing. This flexible tubing allowed substrate changes to be made without breaking vacuum tight water seals.

6.1.2.3.3 Experimental Results.

Initial results from the sputtering deposition of films of mixed oxide materials were encouraging but indicated that higher substrate temperatures should be used in order to produce denser, more conductive films. Layers of the interconnection material, $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$, were deposited onto both alumina and zirconia substrates. Some problems were encountered in the deposition onto the porous zirconia. 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 showed a "smooth" surface and usually "flaked" off the substrate when scraped. This indicated the weakest point of this structure is the alumina/lanthanum chromite interface with the lanthanum chromite 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 ZrO_2 . The first attempt was to electrically isolate the zirconia to provide for 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 did seem to improve the mechanical integrity of the film somewhat.

However, the most likely cause of poor film structure appears to be contamination of the substrates. This was finally alleviated by a 12h, 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.

Initial results on low-temperature depositions, with the substrate unheated, indicated that adequate conductivity levels could be obtained in the sputtered films by heating them in air to 1000°C. Conductivities of these films were equivalent to those of the bulk material.

The films, as deposited, appeared non-porous, but became porous after heating. The heating in air appeared to be crystallizing the film, causing the structure to open up.

Depositing at a higher substrate temperature normally produced a better film, since the deposited atoms have a higher energy, allowing them to diffuse readily over the surface of the film. This produced a denser film with a higher degree of crystallinity. This can be seen in the x-ray powder patterns of the interconnection material, $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$, shown in Figure 6.10. The pattern (a) was obtained from deposition made onto an unheated substrate. However, there is some heating from the plasma and the temperature at the end of the run was approximately 215°C. The lack of any structure indicates that this film is amorphous. The film-deposited at a higher substrate temperature is shown in pattern (b). The substrate was heated to 400°C during deposition. This pattern should be compared to the pattern of d, which is the starting powder.

The anomalously strong line for the (100) plane, together with its shape indicates a preferred orientation with the <100> directions perpendicular to the surface. The width of the line indicates a smaller crystallite size in (b), as compared to the starting powder.

Fig 6.10 X-ray Powder Patterns of $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$
Interconnection Material Deposited by RF Sputtering

- a) 100 watts RF Power, $T_s = 215^\circ\text{C}$
- b) 250 watts RF Power, $T_s = 400^\circ\text{C}$
- c) Sample b, fired at 1000°C for 1 hr
- d) Starting powder

After firing (b) at 1000°C in air for one hour, the sharpness of the lines in (c) indicates a crystalline size the same order as the starting powder. The intensity indicates that the preferred orientation still exists and the columnar growth pattern of the film still exists.

Observation of the films with the scanning electron microscope (SEM) (see Section 10.3.1) indicates that those deposited at temperatures over 400°C are considerably less porous, even after heating, than those grown at lower temperatures. This indicates, from the above x-ray data, that the recrystallization is the primary cause of the cracking. The required temperature for the optimum film properties has not defined but appears to be over 400°C.

Table 6.2 summarizes the depositions from Run 17 to Run 25. The most significant change made during these runs was the addition of oxygen to improve the stoichiometry. The deposited 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 6.2, the addition of oxygen eliminated this problem. In addition, the films had a more uniform appearance. Run No. 21, made 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. 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 showed flaking, with the separation occurring within the bulk of the film and not at the film-to-substrate interface. This may have been due to internal stresses caused by non-stoichiometry or contamination during the run. Severe outgassing could have occurred 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 was monitored and

TABLE 6.2
SUMMARY OF RF SPUTTERED $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$ Films
Y

Run No.	Samples	RF Power Input	Substrate Temperature	Ambient	Time	Comment(s)
17	Al_2O_3 (1) ZrO_2	350 W	450°C	Argon	7 hr	This 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 μ). 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.

this consisted of added argon, even 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 was only severe at high substrate temperatures (600°C) and high deposition rates. It did occur at lower temperatures but was considerably reduced, since substrate temperatures of 450°C appeared adequate to produce dense layers. In addition, a lowered deposition rate at this lower temperature also helped to produce a smoother film. The standard conditions for deposition were set at 200 watts RF power input with a substrate temperature of 400-450°C. These conditions did not produce a good film on every run, but the yield (50 to 75%) did appear 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 appeared 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 was to smooth out the surface of the target prior to each run and add fresh powder if needed, but this did not appear sufficient to eliminate the problem. A hot pressed target of this material was fabricated, hopefully, to cure problems associated with the powder target. However, additional problems (such as cracking due to uneven heating) might occur to the hot pressed target.

One run was completed using the hot-pressed target. This was a low power deposition (100 watts) to determine the performance of this target. The deposited layer did appear more uniform than did the samples from similar runs made with the powder target. In this run, the substrate temperature was 500°C and total time was 18 hours, which produced a thin film (3-5 microns). Additional depositions are required at higher power and longer times to verify that the nonuniformity can be eliminated.

6.1.2.3.4 Heat Treating and SEM Examination of RF Sputtered Interconnection Film.

Lanthanum chromite films produced by RF sputtering provided our first thin layers for study. This technique produced layers of the same composition as the (single phase) lanthanum chromite target and produced dense layers. Compared to the EVD technique, however, it was slow and the film was sensitive to contamination of the surface on which it was formed. The films varied in crystallinity, depending on the substrate temperature during deposition. Unless deposited on a heated substrate (e.g., 450°C), the lanthanum chromite was non-crystalline (to x-ray diffraction), and subsequent heating to 1000°C caused films to crack in a water-hydrogen but not an oxidizing (air) atmosphere for the case of $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$. A typical crack which formed during a subsequent 1000°C anneal is shown in Figure 6.11. This figure shows an SEM pattern of $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$ deposited on a nickel-zirconia cermet fuel electrode. A film deposited simultaneously on an indium oxide electrode, but heated in air, did not crack. The crystallization process was apparently affected adversely by the hydrogen/water atmosphere. This might be due to a slight reduction in the oxygen content of the lanthanum chromite, which, in turn, changed the electrical conductivity of the oxide. This phenomenon may be related to the nucleation and growth phenomena necessary for crystallization, wherein a tendency for non-uniform or two-phase nucleation results in localized crystallization strains. On the other hand, $\text{La}_{.95}\text{Mg}_{.05}\text{CrO}_3$, which is not stabilized against the orthorhombic to rhombohedral phase transformation by aluminum addition, was probably more subject to simultaneous nucleation of two crystalline forms. It has, in fact, been observed to crack during heating (to crystallize) even in air.

We may conclude that dense uncracked films of lanthanum chromite doped with Mg^{2+} and Al^{3+} , stable at 1000°C, can be made either by (1) the RF sputtering technique, provided we use substrates heated to least 450°C or (2) in some instances, merely annealing non-crystalline films in an oxidizing (e.g., air) atmosphere.

A B C

10 micrometers

1. As sputtered

A B C

10 micrometers

2. Annealed at 1000°C in
H₂/H₂O = 2.5 for 4 hours

A B

10 micrometers

3. A Cracked area in annealed film

Fig 6.11 $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$, RF Sputtered on a Porous Nickel Cermet Fuel Electrode at $\sim 300^\circ\text{C}$
(A) $\text{La}_{.95}\text{Mg}_{.05}\text{Cr}_{.75}\text{Al}_{.25}\text{O}_3$; (B) Porous Nickel;
(C) $(\text{ZrO}_2)_{.9}(\text{Y}_2\text{O}_3)_{.1}$

6.1.2.3.5 Summary.

In general, interconnection films can now be produced by RF sputtering. The early results indicated that the conductivity levels obtained with these sputtered oxides, after heat treatment, were close to the values of the bulk material. The as-deposited films were quite dense but had a low conductivity. Heating the films in air (1000°C) increased the conductivity but also produced some cracking of the film. This was apparently due to a recrystallization occurring during the heating. Raising the substrate temperature during deposition improved this, and deposition temperatures of 400-500°C appeared sufficient. The films produced at these temperatures are somewhat crystallized during the deposition and the subsequent heating does not adversely affect them.

Problems involved with the deposition at these temperatures were associated with a lack of uniformity. The films lacked integrity in some areas, although film to substrate adhesion was good. The cause of this has not yet been determined but outgassing from the powder target is a primary suspect. This should be eliminated with the use of a hot-pressed target.

6.1.3 Subtask 1C. Development of Other Stack Components

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

6.1.3.1 Fuel Electrode Development

Nickel-zirconia cermet electrodes were the sole type of fuel electrodes presently considered in our studies. These electrodes were used in the 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.

6.1.3.2 Air Electrode Development

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

6.1.3.3 Solid Oxide Electrolyte Development

Yttria-stabilized zirconia (~ 10 mol % yttria $\pm 2\%$) was the preferred solid electrolyte composition that was used in the preparation of multicomponent thin film tests and was used in the fabrication experiments and in the fuel cell stack tests. Presently, no other electrolytes appear as promising and, therefore, no further solid electrolyte compositional development work was undertaken on the program.

6.2 TASK 2. FABRICATION TECHNIQUES

The purpose of this task was 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 was to optimize the fabrication of the electrodes and substrate components.

6.2.1 Subtask 2A. Interconnection Fabrication

Fabrication techniques that have been considered during the program for the interconnection materials included radio frequency (RF) sputtering and electrochemical vapor deposition (EVD). As the program continued the RF sputtering technique was used for preparing films for physical and chemical property evaluations. Work for fabricating the interconnection film as an actual fuel cell component then centered on the EVD technique for fabricating modified lanthanum chromite interconnection films.

6.2.2 Interconnection Fabrication by Electrochemical Vapor Deposition (EVD)

6.2.2.1 Introduction

RF-sputtering has been useful as a technique to prepare test samples for determination of materials properties of thin interconnection layers during the program. However, it is hard to imagine that RF-sputtering will be a viable fuel cell fabrication technique, due to the low film growth rate and the complexity introduced to the process by the tubular shape of the cell stack-substrate (which, in all probability, needs supportive heating).

Electrochemical vapor deposition (EVD) is believed to be a viable method for the preparation of oxides, in addition to the solid electrolyte, for which it was developed. As described in detail for the fabrication of yttria-stabilized zirconia⁽⁹⁾ one can expect film growth, also, if the oxide exhibits predominantly electronic conductivity and, to a very minor extent, oxygen ion mobility. As a matter of fact, one should expect film formation, even if both electronic and ionic mobilities are low, as observed from scale formation in the oxidation of metals.

The ultimate proof for the viability of EVD as a method for oxide layer formation would be the growth of alumina (α - Al_2O_3) layers, since it is known that alumina acts as a good insulator, up to high temperatures.⁽¹⁰⁾ We formed 5 μm thick layers of α - Al_2O_3 by EVD over a porous Al_2O_3 -tube at 1300°C. The deposition was accomplished by flowing AlCl_3 vapors around the tube, while the inside was exposed to a 1 to 1 mixture of hydrogen and water vapor at a reactor pressure of nearly 1 mm Hg.

This very encouraging experiment raised the hopes for growing more complex oxides that show promise as interconnection materials. Rare earth chromites show some promise, however, it is known that the fabrication of dense specimens of these oxides is extremely difficult. We initially prepared yttrium chromite layers by EVD. In each experimental run we were able to produce dense layers, however, these layers consisted predominantly of yttrium oxide, doped with chromium oxide. The reason for this is, probably, that chromium oxide-doped yttria has a higher oxygen ion mobility than the yttrium chromite and, therefore, is the preferred

phase. Another set of EVD experiments were conducted with strontium oxide-doped lanthanum chromite, a material that has been used in the investigation of MHD electrodes. The first deposition run resulted in the formation of a very thin layer (2-3 μm) of a dark green film, that was identified as lanthanum chromite (see Figure 6.11). The deposition was conducted over a porous nickel-zirconia cermet fuel electrode. Very preliminary resistance measurements with a gold electrode on one side and the fuel electrode on the other side confirmed the presence of a well conducting oxide, with a resistivity of less than $10\ \Omega\ \text{cm}$ at 900°C . The lanthanum chromite layer was prepared during a 3 hour run at 1200°C and $\sim 1\ \text{mm Hg}$ pressure. It was expected at that time that the deposition rate would increase with higher temperatures. A new EVD furnace had to be constructed in order to raise the temperature capability over that of the existing equipment. However, the existing EVD equipment allowed the refinement of other process parameters, like preparation and vaporization of metal halide melts for vapor sources, as well as reactor and nozzle arrangement for obtaining long and uniform deposits. Figure 6.12 shows the cross-section of the first lanthanum chromite film produced over a cermet fuel electrode.

The fabrication of a thin lanthanum chromite layer and the unsuccessful attempt to form yttrium chromite by EVD suggested that strontium oxide might not only act as a dopant for achieving higher electronic conduction but also enhance oxygen ion mobility by the creation of vacancies. It was concluded that the presence of strontium oxide might be essential to form the chromite phase, in that it raises the oxygen ion mobility of the rare earth chromite over that of the rare earth oxide and makes it the preferred growing oxide phase. Later experiments with magnesium as a dopant helped to further clarify the growth mechanism of interconnection layers.

6.2.2.2 State-of-the-Art of Interconnection EVD

A new high temperature reactor and reactor furnace were assembled during the program. This was necessary for the deposition of modified lanthanum chromite films at higher temperatures. Two other existing

Fig 6.12 Cross-section of a lanthanum chromite film over a nickel-zirconia cermet fuel electrode (1100x).

reactor assemblies allowed deposition temperatures of only 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 $\mu\text{m/h}$).

The new reactor furnace has a 0.6 m long hot zone that reaches 1600°C at the maximum. The furnace is of the silicon-carbide, glow bar-type and is equipped with a low-density alumina felt insulation that allows rapid heating (1-1/2 hours from RT to 1350°C), so that a total deposition run of three hours duration can be accomplished during eight working hours.

The total system has been operational and runs have substantiated the expected increased growth rate of lanthanum chromite films at higher temperatures. In recent depositions, a reactor set-up according to Figure 6.13 has been used. The outer reactor tube, normally consisting of quartz, was replaced by mullite, to better resist the high temperature and vacuum conditions. Inside reactor linings of graphite have been maintained.

The arrangement of the substrate tube in the EVD reactor is shown in Figure 6.13, indicating how chlorides of chromium, lanthanum and strontium (or magnesium) 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 Figure 6.14, 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.

Experimental difficulties were experienced in attempting to grow thick layers of lanthanum chromite. Some of these difficulties were associated with an air leak in the vacuum assembly (discovered to be a minute cut in a rubber supply hose, that caused leakage in a certain

Fig. 6.13 — Reactor arrangement for EVD of Sr-doped LaCrO_3 interconnection films at temperatures above 1200°C

- 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. 6.14 —Arrangement of substrate tube and holder for electrochemical vapor deposition of electrolyte and interconnection-oxide films

position, yet did not show up in pre-run leak tests). Considerable more process difficulties were encountered in trying to dope the lanthanum chromite for conductivity, by introducing alkaline earth element oxides.

Thermodynamic considerations showed that the introduction of alkaline earth elements into the oxide phase is problematic if the starting materials are the chlorides of these elements. These alkaline earth chlorides are thermodynamically more stable than the alkaline earth oxides, so that a voluntary incorporation into the lanthanum oxide cannot, normally, be expected. The only method to include these elements was by shifting of the equilibrium of the chemical reactions into the more favorable direction of oxide formation. This was finally achieved by the application of a considerable excess of magnesium chloride to the vaporized halides. The ratios of lanthanum to magnesium to chromium in the EVD reactor were approximately 1:2:3, versus 1:0.02:0.98 in the deposited film of lanthanum chromite (see Section 6.22.1). This ratio of chlorides was established by methodically changing halide ratios. The incorporation of magnesium was first noted by a sudden increase in growth rate of the layer, indicating increased oxygen ion nobility yet the reduction of room temperature resistance was still unnoticeable. Successive increases of $MgCl_2$ concentration and reduction of $LaCl_3$ concentration in the vapor phase resulted in noticeable room temperature conductivity and further increased growth rate. The deposited films were dense and further process development was temporarily terminated. Emphasis was then directed toward incorporating such an interconnection film into a fuel cell stack.

At this stage of the process development, the following conditions have been established for the formation of dense, magnesium-doped lanthanum chromite interconnection film, as can be seen in Figure 6.12:

temperature:	1350°C
pressure:	0.1-0.5 mm Hg
La/Mg/Cr ratio:	1:2:3
type of halide:	chloride
oxygen activity inside substrate:	$\sim 10^{-13}$ atm (from a H_2/H_2O mixture)
deposition time	1 h

Magnesium-doped lanthanum chromite can be prepared into dense films of 40 to 50 μm thickness, during a one hour EVD deposition run at 1350°C. The growth rate depends on magnesium doping level and temperature. Aluminum can be easily incorporated into the deposit as an impurity (see Section 6.1.2.1) and future attempts to incorporate this element will not face similar problems as the doping with magnesium.

6.2.3 Subtask 28. Solid Electrolyte Fabrication

6.2.3.1 Introduction

Only a few oxides are suitable as electrolytes for high temperature fuel cells, despite the fact, that many new mixed oxides are being considered. Most oxides must be rejected on the basis of chemical instability in a steep oxygen activity gradient of 1 to 10^{-18} atmosphere, or because of considerable electronic conductivity (which causes reduced conversion efficiency). The three candidate host oxides that come close to being practical are: thorium, ceria and zirconia--in doped form for stabilization and/or increased ionic conductivity. Thorium-based mixed oxides were rejected in the program because of insufficient conductivity and handling problems (radiation level). Ceria was rejected in the program because of its electronic conductivity in contact with fuel gas and because of its inferior mechanical strength, although the conductivity at 800°C of gadolinia-doped ceria compares favorably with yttria-doped zirconia at 1000°C. By this eliminating process, doped zirconia remained the only practical solid electrolyte. New developments in this field, however, have been watched and, hopefully, when better, suitable oxides can be found with higher conductivity at lower temperatures, they could be evaluated in a future program.

6.2.3.2 Electrochemical Vapor Deposition (EVD) of Solid Electrolyte

Although the feasibility of this vapor deposition process has been proven by fabricating electrolyte layers for cells that operated at

a current density level of over 500 mA/cm² without undue voltage loss caused by electrolyte resistance, many EVD process parameters and electrolyte characteristics remained to be investigated.

During the program, we focussed our attention on determining the growth rate of the electrolyte under process conditions used in the past. Figure 6.15 shows the principle of film growth.

Figure 6.15 Scheme of Oxide Film Growth by EVD

The film grows over a porous substrate, in the case of this fuel cell, over the nickel-cermet fuel electrode. Figure 6.15 shows only a porous substrate for simplicity sake. Two different phases in film growth can be observed. The first phase is characterized by the simultaneous chemical reactions,

and

that result in the formation of a mixed oxide of zirconium and yttrium in the pore vicinity. This phase comes to a conclusion when all pores are closed with reaction product. Further film growth can take place only by the movement of ions and electronic charges. Since the reaction product of phase 1 is an ionic conductor with minimal electronic conductivity, one can write the simultaneous electrochemical reactions that occur during phase 2 of film growth as follows:

These equations represent sum-reactions, however, intermediate reaction steps may or may not precede. This is also the case for Eq. 1 and 2. It must be expected that the reaction products of phase 1 and phase 2 differ in composition and microstructure. We planned the following experiments to shed light into film growth of both phases.

6.2.3.3 Experiments

Porous zirconia tubes (12 mm O.D., 1.5 mm thickness, approximately 30 volume %, open pores of 10 μm or less, of calcia-stabilized zirconia) were dipped into a slurry of yttria-stabilized zirconia powder and butyl acetate, to coat the tube surface with a thin ($\sim 20 \mu\text{m}$) powder layer. These tubes were used as substrates in the EVD, in order to separate the film for analysis. Electrolyte films were grown over separate porous tubes for 15, 30, 120, 180 and 300 minutes. The films were removed from the substrate and were separated from adhering powder by ultrasonic agitation. The film thickness was determined by weighing cleaned film chips from a measured surface area of the 15 and 30 minute runs and by observing cross-sections of the 120, 180 and 300 minute runs. The rate of film growth under given conditions is shown in Figure 6.16.

Fig. 6.16 — Determination of electrolyte growth rate in a typical EVD - Run

The exposure of the thinnest film (15 minute growth) to liquid acetone or water, showed no penetration of the liquid through the film whatsoever, which indicated the absence of fine holes or cracks. It was concluded, that phase 1 of the EVD process was completed very early and uniformly during the run. It was somewhat surprising to find a linear where a parabolic film growth relationship had been expected. The mechanism of film growth can be compared with that of scale formation in the oxidation of metals. Compared with corrosion mechanisms, a linear relationship would indicate the formation of porous films, which is obviously not the case. The following explanation for this behavior is given.

Phase 1 reaction product grows in a relatively high oxygen activity atmosphere, as determined by the presence of water vapor (Eq. 1, 2). The oxygen activity will change drastically during completion of pore closure and further film growth takes place under a lower oxygen activity (Eq. 3, 4). It is expected, therefore, that reaction product of phase 1 exhibits a lower electronic conductivity than that of phase 2, and, depending on the degree of difference, will determine the rate of film growth during phase 2.

It was difficult to determine the thickness of the phase 1 layer because of the porosity of the substrate and partial incorporation of powder particles of the substrate. However, by extrapolation (Figure 6.16), a fictive layer thickness was determined to be 3 to 4 μm . It was assumed that this was also the average pore size of the powder layer of the substrate.

6.2.3.4 Halide Delivery System for EVD of Solid Electrolyte

In the fabrication of solid electrolyte films by the EVD process, the delivery of zirconium and yttrium chloride into the reaction chamber was accomplished by the chlorination of yttria-stabilized zirconia with chlorine in the presence of carbon. This reaction lead to a chloride vapor mixture that had nearly the same molar ratio of yttrium to zirconium as expected in the solid. The reaction occurred at 1000° to 1100°C.

Yttria-stabilized zirconia powder (minus 325 mesh) was ball milled with lamp black (1.5 stoichiometric amount) in a suspension of acetone. Two weight percent of the dry matter was cellulose acetate that was added, predissolved in acetone, as a binder. The slurry was ball milled for 2 hours, filtered and dried. The dried material was broken into grains of 1 to 2 mm size. Finer material was wetted with acetone, dried and reprocessed.

The granular material was filled into a quartz tube which was fitted with graphite wool plugs to prevent the granule bed from falling apart. The tube was evacuated and heated to 1100°C both to drive off organic binder and to strengthen the carbon/oxide granules. After this was accomplished, the bed was purged with chlorine under vacuum to pre-react the granules at 1100°C. Beginning of the reaction was shown by condensation of chlorides in the cold part of the evacuated quartz tube. The granule bed was then cooled under reduced argon or nitrogen pressure (flowing gas) and the resulting material was stored, until used as source material in the chemical vapor deposition for electrolyte.

6.2.3.5 Status of EVD Fabrication of Solid Electrolyte

These investigations showed that the EVD principle of electrolyte film growth was practical and even more favorable than originally expected, in that chemical composition seemed to be close to that of the source material, that linear film growth allowed going to thicker films in shorter times if so desired, and that film densification occurred during the first few minutes of film growth. This unique behavior has not been found by any other known vapor deposition process, if applied to a porous substrate, and is particularly useful in the fabrication of a solid electrolyte fuel cell. EVD can be used, also, to prepare other possible solid electrolytes, when they are identified, as can be expected from the results obtained from successful attempts to grow complex oxide interconnection films by EVD (see Section 6.2.2.2).

6.2.4 Subtask 2C. Air and Fuel Electrode Fabrication

The purpose in exploring fabrication techniques for both the air and fuel electrodes was to optimize their preparation as deposited films of about 20-50 μm in thickness.

The proposed air electrode for solid electrolyte fuel cell stacks is of the composite oxide type. That is a porous zirconia skeleton of same composition and integral part of the solid electrolyte is impregnated with an oxide of electronic and oxygen ion conduction. This porous structure is backed up by a conductive coating of doped indium oxide, that contacts the interconnection of an adjacent cell. This structure was derived from systematic air electrode research in the past* and yields devices with acceptable performance.

6.2.4.1 Fabrication of the Air Electrode Current Collector

At the onset of the program tin-doped indium sesquioxide (In_2O_3) and antimony-doped tin oxide (SnO_2) films were considered as current collector materials for the air electrode of the high temperature solid electrolyte fuel cell. Solution spraying and chemical vapor deposition (CVD) techniques were selected for the application of such films.

6.2.4.1.1 Background.

The performance of air electrodes, although acceptable at the start of this program, needed improvement, with respect to reproducibility of current collector application and introduction of controlled porosity in the collector. These efforts are described in this section. The final fabrication of a total air electrode structure is described in the fabrication of a fuel cell stack in Section 6.3.3.2.5.

Past efforts⁽¹¹⁾ led to the selection of tin-doped indium sesquioxide (In_2O_3) as the best air electrode current collector material. The required properties for this selection were: good electronic conduction, thermal expansion compatible to the calcia stabilized zirconia electrolyte and chemical stability in air at 1000°C. The desired film thickness is 20-50 μm . Antimony-doped tin oxide was considered as an alternate air electrode current collector material in these studies,

since it has been reported that its electrode polarization behavior is superior to that of tin-doped indium oxide⁽¹²⁾. However work on antimony-doped tin oxide was discontinued, mainly due to its low thermal expansion ($\sim 5 \times 10^{-6}$ m/m/°C) at 1000°C.

From considerations of all the components of the fuel film assembly, the operating temperature (1000°C), and gaseous environments of such cells, the techniques employed for the application of the air electrode films should be those with the most controllable variables. Solution spraying and chemical vapor deposition (CVD) were the techniques with promising features for this application. In the case of the spraying technique, an aqueous solution that contained the desired metallic constituents in the appropriate ratio was aspirated via a carrier gas to the direction of the surface of the hot substrate material where the oxide films form. In the CVD technique, vapors of the metallic constituents of the desired oxide film were usually generated by evaporation of a substance or by reaction of a vapor source material (i.e., metals or their oxides) with an active transport agent inside a chamber. These vapors were carried via a carrier gas to the deposition zone where oxide film formation occurred from the oxidation and/or hydration of these metallic bearing vapors. Oxygen and/or water vapor required for the reaction was independently supplied via a gas distributor in the vicinity of the deposition target.

6.2.4.1.2 Tin Chloride - Indium Chloride Solution Spraying.

Based on the tests conducted in the program, the following observations were made, regarding the indium and stannous chloride solution spraying techniques. In order to obtain In_2O_3 films of acceptable thickness, the solutions had to be atomized at the target directly into the hot reaction chamber. However, when this was done, the rapid depletion of reagents in the gas stream yielded a concentration gradient and resulted in non-uniform air electrode layers. To prevent non-uniformity of the deposit about the target circumference, geometric arrangements with spraying become critical and had to be carefully adjusted. This spraying approach always involved two inherent traits: the potential

thermal shock from wet droplets impinging upon a heated substrate tube and considerable waste of reagents. Therefore, the solution spraying approach was abandoned in favor of the CVD technique.

6.2.4.1.3 Chemical Vapor Deposition (CVD) of Tin Doped-Indium Oxide Films.

Figure 6.17 shows a side vertical cross-section of the experimental arrangement employing an HCl/NH_3 gas mixture.

The components of this reactant gas mixture (HCl and NH_3) were supplied directly from the gas cylinders into a joint line that was heated close to 340°C . The mixture was carried with a N_2 -carrier into the tin-doped indium oxide (In_2O_3) fixed bed reactor A, via the ejector B. The volatile reaction products inside reactor A are tin and indium bearing species. In the prevailing atmosphere of chamber A these vapor species were expected to be various chlorides, oxychlorides and oxyhydroxides. As was mentioned above, these volatile species were conducted to target tube T, where the formation of the tin-doped indium oxide occurred at a temperature of $850\text{--}900^\circ\text{C}$ with the aid of the O_2 /moisture ejector C. The moisture was introduced by passing the oxygen gas carrier through a water bubbler maintained at a temperature of about 85°C . Moisture-containing nitrogen gas was also passed through the ejector C and resulted in oxide film formation on the target. However, the water vapor/oxygen mixture was preferred because it yielded oxide deposits of somewhat lower electrical resistivity. The relative position of the target tube (i.e., T_1 or T_2 , etc.), with respect to the upper end of the vapor source reactor A and the nitrogen gas flow rate inside the reactor, have been shown to be variables influencing the thickness of the films. For example, the target position T_2 on Figure 6.17 resulted in thicker deposits and shortened the time of their formation. This was a consequence of the higher reactant vapor density at this position. A persistent problem, contributing to non-uniform deposits, involved the uneven distribution of the carrier gas (N_2) and reactant mixture (HCl/NH_3) throughout the granulated bed of the tin-doped indium oxide sample inside Chamber A.

Fig. 6.17 — CVD Apparatus: Indium oxide-ammonium chloride reactants (using NH_3 - HCl gases)

6.2.4.1.4 Results.

The configuration of Chamber A (see Figure 6.17 double tube connection) extended the height of the bed and gave better deposits on the tubular targets. The best results that have been obtained were with this chamber. Visual reproducibility of the thickness and length of the deposits, however, was only obtained when the experiments were repeated with freshly granulated tin-doped indium oxide sample inside chamber A and the height of the sample extended almost to the upper end of the chamber. The duration of such successful experiments was ~40 minutes and yielded films of adequate thickness (i.e., $\geq 50 \mu\text{m}$) over a length of 20 to 25 cm on the substrate zirconia tube. The target tube was incrementally rotated during deposition.

Two micrographs that illustrate the degree of reproducibility of the films are shown in Figure 6.18. The measured film thicknesses in these two runs were: $56.5 \pm 10.5 \mu\text{m}$ and $65.0 \pm 8.5 \mu\text{m}$, with the difference of these two deposits within the lengthwise film thickness variation of each deposit.

The temperature dependence of the resistivity of a SnO_2 -doped- In_2O_3 film on a zirconia target was measured using the four probe technique (ρ/δ , $\frac{\Omega \text{ cm}}{\text{cm}}$). The results are shown in Figure 6.19. This particular film had an average thickness of $\sim 80 \mu\text{m}$. Generally, ρ/δ increases by a factor of about 1.7 from $0.27 \Omega\text{-cm/cm}$ at room temperature to approximately $0.43 \Omega\text{-cm/cm}$ at 600°C , then drops to $0.20 \Omega\text{-cm/cm}$ at 1000°C . This same general behavior has been observed elsewhere⁽¹³⁾, as shown in Figure 6.20. Here the ordinate scale has been adjusted to roughly fit our own for comparison purposes. Various explanations for the curve shape have been given⁽¹³⁾, but Figure 6.19 represents the type of curve one should expect.

Finally, if one uses the average film thickness of $80 \mu\text{m}$ from the In_2O_3 film measured in Figure 6.18, then at 1000°C , one can calculate the resistivity of the SnO_2 -doped film to be $1.6 \times 10^{-3} \Omega\text{-cm}$.

Fig 6.18 Photomicrographs of SnO₂ doped In₂O₃ on Zirconia Substrate (200x).

Fig. 6.19 — Resistivity per unit thickness (ρ/δ) vs temperature ($^{\circ}\text{C}$) for SnO_2 doped In_2O_3

Fig. 6.20 — Resistivity vs temperature (°C) for In₂O₃ (Ref. 3)

The development of the air electrode current collector continued with the chemical vapor deposition (CVD) of tin-doped indium oxide films. In the first annual report, several new design features of the experimental arrangement were described.⁽¹⁴⁾

6.2.4.1.5 CVD Apparatus - Refinement Details

Figure 6.21 shows the entire arrangement that was used in the CVD experiments.

Figure 6.22 shows one end view (not yet closed) of the alumina chamber of Figure 6.21. The perforated ceramic plate (LAVE, Guide H) shown here was another added feature and ensured continuous, uniform flow distribution of the $N_2/HCl/NH_3$ incoming gaseous mixture over the oxide sample. Such a flow distribution should be maintained over the entire oxide sample bed height and length. This can be realized only if a uniform sample shape and size is used and maintained, during the course of each chemical vapor deposition experiment. For this purpose, the oxide samples were pelletized to fixed size. The pellets were made with an F. J. Stokes tablet machine (Serial No. T-39504). Figure 6.23 shows a magnified photograph of these uniform pellets [actual size: 1/8" (3.2 mm) OD by 3/8" (9.6 mm)L].

It was found that the procedure employed for the preparation of the initial intimate mixture of reactant oxide powders was critical, in obtaining proper flow characteristics necessary for the successful formation of these small pellets. 2 wt % of cellulose acetate was the added binder to the acetone slurry of the tin-doped indium oxide mixture. This slurry was ball milled for 1 hour. It was transferred to a dish and slowly heated to vaporize the acetone. The resulting powder cake was crushed through a screen.

Once the pellets were formed, they were preheated to about 600°C in air in order to remove the binder. Pellet consolidation by sintering of the tin-doped indium oxide was achieved by heating in air at 1500°C for 17 hours.

Fig 6.21 Experimental Arrangement for the Chemical Vapor Deposition (CVD) of Indium Oxide and Tin-Oxide Air Electrode Current Collector Films

Fig 6.22 End-view (not yet closed) of the Alumina Chamber of the CVD-Reactor Shown in Figure 7.

Fig 6.23 Pellets of Reactant Oxide Sample (Mag. 2X)

6.2.4.1.6 Results with Refined Apparatus

The reactant oxide and target tube temperatures in the CVD system were 650°C and 850°C, respectively. Reproducible, tin-doped indium oxide films were obtained initially on alumina target tubes (1.27 cm OD). The total vapor exposed section of each tube was 25 cm long and the duration of each experiment was 60 minutes. The weights of three such films were 3.164, 3.100 and 3.071 gms. Figure 6.24 shows the coated alumina tube and the measured room temperature film resistivity over thickness (ρ/δ , Ω -cm/cm) profile for these three films. The constancy of these ρ/δ values over the entire vapor exposed length (25 cm) illustrates the desired uniform film thickness and reproducibility. These results allow the calculation of the film thickness (δ) from the film weight, density of indium oxide, and the covered area of each target tube. Calculated values were within the desired range (20-50 μ m). The first of these tubes was cycled three times between room temperature and 1000°C in air. During the third cycle, it was allowed to anneal for about 72 hours at 1000°C. The final measured, ρ/δ -value at 1000°C at the end of this annealing period was 0.11 Ω -cm/cm. From the calculated δ -value (44.2 μ m), a ρ -value of 4.9×10^{-4} Ω -cm was obtained.

Thermal expansion measurements on a sintered specimen of tin-doped indium oxide are shown in Figure 6.25. This specimen was fired at 1500°C prior to these measurements. The coefficient of expansion at 1000°C, as obtained from these measurements, is 8.95×10^{-6} m/m/°C and compares with the latest literature value of 9.5×10^{-6} m/m/°C for In_2O_3 .⁽¹⁵⁾ These data give additional support to the original view that indium oxide should be the preferred current collector material for the air electrode.

Therefore, the improvement in the design of the CVD reactor and the preparation procedure for the reactant oxide samples resulted in the formation of reproducible, tin-doped indium oxide films over the entire vapor exposed length ($\sim$ 25 cm) of tubular targets (1.27 cm OD). Desired film thickness (20-50 μ m) and resistivity values ($\sim 10^{-3}$ Ω -cm) were achieved.

Fig 6.24 Resistivity Profile of Tin-doped Indium Oxide Films on Alumina Tubes from Three Successive CVD Experiments.

(a_L , a_R : Current probes; 0 Run, sample IN_{II} -1; + Run, IN_{II} -2; o Run, IN_{II} -3)

Fig. 6-25. Thermal Expansion of a Pressed Specimen of Tin-Doped Indium Oxide, Previously Heated at 1500°C for 17 Hours

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 experiments are shown in Figure 6.26. For Experiment No. IN_{II}-4, the fourth in succession of the above mentioned experiments, a Westinghouse made zirconia target tube was used. The ρ/δ vs distance profiles of the other four experiments shown in Figure 6.26 constitute two separate duplicate sets (i.e., IN_{II}-5/IN_{II}-6 and IN_{II}-7/IN_{II}-8). These data show satisfactory overall reproducibility.

Resistivity ($\Omega\text{-cm}$) measurements on the reactant oxide material were also carried out on a sintered (1500°C in air for 17 hours) square bar specimen of tin-doped indium oxide. The dimensions of this bar specimen were: 4.8 x 0.82 x 0.93 (cm). The bar had been prepared using conditions identical to those used for the pelletized reactant oxide samples.

The ρ ($\Omega\text{-cm}$) values of the bar specimen ranged from 1.5×10^{-3} to $\sim 8.0 \times 10^{-3}$ between room temperature and 1000°C. This magnitude of change provided indirect proof of solid solution formation between SnO₂ and In₂O₃, under the conditions that the reactant oxide pellets are prepared. Independent evidence of solid solution formation came from microscopic examination of the pellets and their complete solubility in a HCl/HNO₃ solution, where it is known that free SnO₂ is not soluble.

The average ρ/δ values of some of the films at room temperature and 1000°C were used to obtain their ρ ($\Omega\text{-cm}$) values. These values together with those for the film thickness δ (μm) are given in Table 6.3. The calculated δ in this table was obtained from the film weight, density (7.17 g/cm^3) and area on the target. This calculation assumed uniform deposits along the entire coated length of the target tube. The measured δ values were obtained from micrographs of the size shown in Figure 6.27. These micrographs are typical of many taken along the length of the target tubes of Run Nos. IN_{II}-1 and IN_{II}-4. They demonstrate the impervious nature of the deposited films and the smoother surface of the alumina tubes (a) than that of the zirconia tubes (b) that were made at that time by Westinghouse. For each micrograph of the size shown here, 24 equidistant δ measurements were taken and the average value of each location

Fig 6.26 Resistivity Profile of CVD Tin-Doped Indium Oxide Films on Ceramic Target Tubes.

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

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

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

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

TABLE 6.3

FILM THICKNESS, RESISTIVITY AND CHEMICAL
ANALYSIS DATA OF AS-PREPARED FILMS OF
AIR ELECTRODE CURRENT COLLECTOR

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 6.27 Micrographs showing the type of films obtained from CVD Experiments 1 (a) and 4 (b).

[Average film thickness: (a) 47.0 μm; (b) 38.6 μm].

that was photographed was recorded. The figures in the table, i.e., 47.0 μm and 38.6 μm , are the average of 3 and 8 locations along the target tubes of runs IN_{II}-1 and IN_{II}-4, respectively. The agreement between the calculated and measured δ values is 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 analyses of the films of the four successive experiments are also listed in Table 6.3. The weight percentage 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 6.3 (i.e., 240 minutes). The average weight percentage values of Sn and In of these pellets before exposure were: 1.70 and 82.4, respectively. The corresponding average weight percentage 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 and the chosen CVD-conditions were satisfactory.

The previously reported 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 $8.95 \times 10^{-6} \text{ m/m/}^\circ\text{C}$. 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,⁽¹⁶⁾ and closer to the value of stabilized zirconia--the major stack component.

Electrical resistivity, ρ , measurements of films deposited on stabilized zirconia substrates were obtained as a function of temperature, after an initial anneal in air at 1000°C for more than 120 hours. A reversible behavior in the heating and cooling ρ vs T curves was noted. Typical results of such a behavior are graphically shown in Figures 6.28 and 6.29. 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 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.

6.2.4.1.7 Film Growth Using Seeding

CVD exploratory experiments were conducted that 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 part of this tube area 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 Figure 6.30. 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 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 seeding. 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 Figure 6.30. 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

Fig.6. 28-Resistivity versus temperature behavior of tin-doped indium oxide film deposited on bentonite doped calcia stabilized zirconia tube

Fig.6. 29-Resistivity versus temperature behavior of tin-doped indium oxide film deposited on calcia stabilized zirconia tube [film thickness: 27.8 μm]

Fig 6.30 Resistance Profile of Tin-doped Indium Oxide Film across Seeded and Non-seeded Sections of Calcia-stabilized Zirconia Tube (Run # IN_{II}-11).

accidental gas stream entrainment of powder of the tin-doped indium sesquioxide from the chamber of the reactor. Such entrainment occasionally occurred in the early series of experiments when the vapor source oxide sample was used in the granulated form.

The idea of providing an initial film nucleation site 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. Film thicknesses of ≥ 20 μm were obtained, but 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 μm film thickness was obtained. Visual observations of this thin film indicated porosity due to seeding. Additional vapor deposition was carried out on this tube and a final thickness of 33.9 μm was reached. At this thickness, the film was impervious. Good adherence of the seed powder on the substrate surface is mandatory before its exposure to the reactant gaseous mixture of the vapor deposition process. The conditions for providing such grain seed adherence on the substrate must be improved.

In some of the CVD-experiments unknown variables in the CVD reactor resulted in isolated, band type porous film areas on the zirconia substrate. Figure 6.31 is a micrograph of such an area that 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.

Fig 6.31 Porosity of Tin-doped Indium Sesquioxide Film Caused by Unknown Variable(s) During Chemical Vapor Deposition.

6.2.4.1.8 Summary

Long-time annealing in air at 1000°C of chemically vapor deposited tin-doped indium oxide films on zirconia substrates produced reversible behavior in their electrical resistance upon heating and cooling. Improvements of the air electrode fabrication technique has been accomplished through investigation directed toward a uniform indium oxide current collector and crystal seeding methods to yield porous collector layers by chemical vapor deposition.

6.2.4.2 Fabrication of the Fuel Electrode

6.2.4.2.1 Introduction

State-of-the-art fuel electrode technology, as existed at the beginning of this program, needed improvement in order to achieve two major goals:

1. develop a stronger nickel-zirconia cermet structure, to achieve a better bond to other cell components--especially to the interconnection layer and to the support tube (This can result in reducing the degree of "lifting off" and cracking of interconnection layers due to thermal expansion mismatch),
2. develop a process for fabricating banded fuel electrode layers that eliminates exertion of mechanical forces on the porous support tube by scraping, cutting of masking layers, sand-blasting (to avoid initiation of cracks in the support tube structure that will result in rupture of the entire cell stack even with moderate internal stresses, which could otherwise be tolerable).

6.2.4.2.2 Development of a Strong Nickel-Zirconia Fuel Electrode

The electrode layer consists of a continuous phase of nickel, interlocked in a continuous layer of yttria-stabilized zirconia, so as to render a solid phase of 40 volume % nickel and 60 volume % zirconia. The electrode layer contains nearly 30 volume % voids. This structure is

obtained by cosintering of zirconium oxide and nickel oxide at 1600°C and reduction of nickel oxide at 1100 to 1200°C with hydrogen. Theoretically, the reduction temperature can be a maximum of 1453°C (the melting point of nickel). However, from previous experience, it was observed that the nickel phase became discontinuous due to nickel agglomeration, if the reduction temperature was higher than 1200°C. It was assumed, initially, that this is caused by a wetting problem, aided by sintering forces. Due to the fact that, during cooling to 1200°C the mixture of NiO and ZrO₂ is highly stressed, the zirconia skeleton cracks and results in a weakened structure, after NiO reduction to Ni. It was concluded, that a reaction of small amounts of H₂S with nickel created a low melting metal-sulfide phase that caused the agglomeration of the nickel phase and its discontinuity. The H₂S was evolved from porous ceramic supports under the influence of hydrogen. The problem has since been resolved and nickel oxide reduction is now performed at 1350°C, routinely, leading to a stronger porous cermet electrode.

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 were to be investigated in the program, if necessary, to enhance the fuel electrode conductivity.

Fuel electrode fabrication, as described 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 Figure 6.32 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).

Figure 6.33 shows the resistance decrease of an electrode if the nickel content of 7 mg/cm^2 is increased by electroplating 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.

6.2.4.2.3 Formation of Fuel Electrode Bands.

The formation of fuel electrode bands is problematic, since the following requirements are to be fulfilled:

1. no mechanical force must be exerted on the support tube, to prevent initiation of cracks,
2. feathering of electrode borders must be achieved to minimize possibilities of crack initiation by sharp edges,
3. sufficient structural strength must be maintained at electrode borders, because stresses build up, especially in these areas, due to stack component overlapping.

- 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. 6.32 — Arrangement for nickel plating of fuel electrodes

Fig. 6.33 — Fuel electrode resistance changes with temperature and reduction of resistance by electroplating

In the past, an electrochemical etching process was developed that fulfilled these requirements. However, the masking process that was used required the cutting of heat shrinkable tubing, that had been pre-shrunk over the entire fuel electrode coated support tube. This sleeve was cut with a sharp-edged tool in the area where the electrode was to be removed by etching. Therefore, the masking operation had to be altered both to simplify the masking and etching operation and to eliminate mechanical abuse of the porous support tube.

The etching process is shown schematically in Figure 6.34.

A graphite rod, inserted into the tube, served as the anode. The cathode may be a nickel screen, surrounding the entire tube. A strong electric field was created in the unmasked area, leading to nickel dissolution uniformly in this region throughout the electrode structure.

An etching apparatus was constructed and tested. It makes individual tube masking superfluous and can be used for long stack tubes. The new method resulted in the formation of good quality fuel electrode bands. The device is shown schematically in Figure 6.35.

Here, the stack tube was rotated via the tape transmission, where the tapes were impervious and slightly elastic. The tapes were properly spaced and acted also as masking, over half the circumference of the tube. The graphite rod on the inside of the rotating stack tube and the graphite rod on the outside served as electrodes. A tray with electrolyte was raised into position to establish electrolytic conducting passages between the graphite rods, in those areas that were not masked by the transmission-masking belts. In our experimentation we operated with a current density of up to $2\text{A}/\text{cm}^2$ (exposed fuel electrode area) for 6 minutes in an electrolyte of 5 molar ammonium sulfamate solution. Other aqueous solutions, as ammonium sulfate, ammonium chloride or ammonium hydroxide, can also be used.

Figure 6.34. Etching Method for Nickel-Cermet Electrode

Figure 6.35. Apparatus for Fuel Electrode Etching

The removal of the nickel phase in the electrode structure facilitated the removal of the remaining ceramic skeleton. This was accomplished in a following operation, by liquid honing with a jet of a water-alumina powder slurry. This method was slightly abrasive, however, in a way that did not harm sub-laying structures. A final rinse with deionized water in an ultrasonic cleaner, followed by drying, concluded the fabrication of fuel electrode bands.

6.2.4.2.4 Summary

During this program, major progress was made in creating mechanically stronger nickel-cermet fuel electrodes and in developing a new electrochemical etching technique to produce fuel electrode bands on porous support tubes. The porosity of the support tube is a major parameter in the electrochemical etching process of the nickel-cermet electrode and new in-house developed, highly-porous support tubes allow the fabrication of well defined fuel electrode bands.

6.2.5 Subtask 2D. Fabrication of the Porous Support Tube

The purpose of this task is to develop extrusion technology to fabricate porous, thin wall support tubes of stabilized zirconia $(\text{ZrO}_2)_{.85}(\text{CaO})_{.15}$ for the thin film/fuel cell power generating system.

Porous calcia-stabilized zirconia support tubes are stable in the operating environment of the fuel cell battery and provide the necessary electrical insulation and structural integrity of the series connected stack of cells.

This section on the subtask of porous support tube fabrication, relates the approaches to materials preparation, processing techniques, equipment, and describes the properties of the thin wall porous support tubes developed during the contract period.

6.2.5.1 Technical Background

Porous support tube technology uses calcia-stabilized zirconia tubing ($\sim 1000 \mu\text{m}$ wall thickness). Historically, problems associated with the fabrication of such tubing involve impurities (sintering aids),

insufficient mechanical strength and non-uniformity of the tube surface structure. At the onset of the program both an "in-house" and a commercial source approach were pursued, to obtain tubing of satisfactory properties for use as a high temperature fuel cell support structure.

The requirements of a porous support tube for a thin film fuel cell operating at $\sim 1000^{\circ}\text{C}$ have been determined by many investigators^(17,18,19). Calcia-stabilized zirconia in the cubic phase has been identified as the material possessing the physical qualities to make a promising substrate, upon which to build a high temperature solid oxide fuel cell. Principal requirements of the porous support tube as a substrate in a thin film fuel cell application are:

1. remain geometrically stable, other than for changes associated with typical thermal expansion⁽²⁰⁾,
2. function as the mechanical support for the battery, while being porous enough to allow diffusion of the fuel gases and their reaction products⁽²¹⁾,
3. exhibit a thermal expansion close to that of stack components⁽²⁰⁾,
4. be chemically compatible with other stack components at high temperatures⁽²⁰⁾.

Fabrication techniques known to produce porous support tubes involve extruding or slip casting mixtures of several different particle sizes of calcia-stabilized zirconia. Extrusion of body preparations with additions of cellulose type materials, that burn out during firing, have also been successful. Pressure compacting of spray dried, calcia-stabilized zirconia powders also show promise in the fabrication of porous support tubes with controlled⁽²¹⁾ porosity and permeability.

The capability of extruding porous zirconia support tubes has been developed in house. In dealing with a non-clay material, such as zirconia, the primary problem was the incorporation of the plasticizer to create an extrudable mixture. The success of the extrusion was not only dependent on the selection of a suitable plasticizer but also on

the proper balance of particle size distribution in the starting powder, mixing techniques, aging procedures, die design, drying techniques and firing schedule.

An extrusion apparatus that can be used to handle small batches (2 kilograms) of any composition has been assembled, as shown in Figure 6.36. It can be used in conjunction with an existing 40 ton C-frame press to extrude tubes vertically. The apparatus allows for the evacuation of the mix material prior to extrusion. Entrapped air is removed by a mechanical vacuum pump connected to the cylinder assembly that holds the extrusion batch material.

6.2.5.2 Support Tube Fabrication Experiments

Preparing and shaping calcia-stabilized zirconia powders into porous tubing (1/2" dia x 0.040" wall thickness) suitable for support tubes of thin film, fuel cell, operating at $\sim 1000^{\circ}\text{C}$, requires careful control of the starting particulate solid materials^(22,23,24) and the proper densification of the powders during sintering^(25,26). Porous support tubes have been prepared by controlling the particle size distribution of the zirconia powders and also in combination with materials that burn out during the final firing process of the ceramic tubes.

6.2.5.2.1 Powder Preparation

Starting powders of calcia-stabilized zirconia $[(\text{ZrO}_2)_{.85}(\text{CaO})_{.15}]$ 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 (as shown in Figure 6.37) was utilized to reduce the calcined material to less than 100 mesh, and reduced to minus 325 mesh in a jet mill as shown in Figure 6.38. 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. Figure 6.39 shows the vibrating sieve shaker.

Fig 6.36 Extruder Assembly

Fig. 6.37. Iler Rotating
Disk Crusher

Fig. 6.38. Troost Pulverizing Mill

Fig. 6.39. Syntron Vibrating Sieve Shaker

Table 6.4 shows the flow sheet of porous support tube fabrication process. The in-house tube fabrication process required all the processing steps from weighing of the starting materials (step 1) to the final firing of the tubes (Step 17). Processing of calcia stabilized powders (ZrO_2)_{.85} (CaO)_{.15} from vendors began with the sieving operation (Step 11) where the powders were classified into different mesh sizes. After the materials were screened and classified into different mesh sizes, each lot was identified and stored in a clean dry container in readiness for the next processing step.

6.2.5.2.2 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), as shown in Figure 6.40, was used to homogenize the material (500 gram batch) to the right plasticity for extrusion. To facilitate handling the 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.

Particle size distribution of the sieve fractions of each lot of materials and extrusion batches were analyzed by the MSA sedimentation analysis as reported earlier, in the 6th Quarter report, in the development of high porosity extruded tube fabrication.

The following is an example of an extrusion batch of 500 grams with calcia-stabilized zirconia powder fractions of 70 w/o (-400 +500): 30 w/o (-500 mesh).

Zirconia powder	86.0 w/o
Organic binder	4.0
Water	9.6
Dispersant	<u>0.4</u>
	100.0

TABLE 6.4

PROCESS FLOW SHEET OF POROUS SUPPORT TUBE FABRICATION

1. Weighing
↓
2. Ball Milling
↓
3. Drying (Partial)
↓
4. Slugging (Disks)
↓
5. Presintering (1780°C)
↓
6. Crushing
↓
7. Pulverizing
↓
8. Ball Milling to Form Slurry
↓
9. Magnetic Filter
↓
10. Drying
↓
11. Screening
↓
12. Blending
↓
13. Kneading
↓
14. Extruding
↓
15. Drying
↓
16. Bisque Firing
↓
17. Final Firing

Fig. 6.40. Baker-Perkins
Kneading Machine

In the kneading operation all the dry materials are added first, followed by liquids and the material was mixed until it became smooth and creamy in texture. The total mixing time was approximately 30-35 minutes. After the kneading process the material batch was weighed and sealed in a plastic bag to prevent moisture loss.

6.2.5.2.3 Forming and Densification

Tubes were extruded using the die setup, as shown in Figures 6.41 and 6.42, 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 3 hours. After the tubes were dried the initial presintering (~1300°C) was accomplished either by "hang firing" in a vertical position or by bedding down in a horizontal position 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.

6.2.5.2.4 Extrusion and Drying

Calcia-stabilized zirconia materials prepared for extrusion were all formulated with 15 mole % (~8 w/o) calcia. The ideal plastic condition for the extrusion batch was determined empirically and by the force registered on the ram of the press before extrusion commenced. A good preparation resulted in smooth extrusion without cracking and did not affect tube dimension during the intermittent stop and go operation. Each length of extruded tube (~24 inches) was cut off with a wire cutter as it was caught and cradled in a grooved catcher. Then the grooved wooden sample holders were placed in the humidity oven chamber until the tubes were dry and self-supporting, before transferring to the grooved aluminum samples holders for sintering.

Fig. 6.41. Extrusion die set up with 500 gram capacity of material equivalent to 5-6 feet of extruded tubing.

Fig. 6.42 Extruded die set up for 1000 gram capacity of material equivalent to 10-12 feet of extruded tubing.

Figure 6.43 shows the core pin assemblies for three different hole sizes. The die design was modified to extrude porous tubes with three different wall thicknesses (0.040, 0.050, and 0.060 inch), while maintaining a 0.500 inch outside diameter. Figure 6.44 shows the major individual parts of the die assembly after it was modified to accommodate a larger batch size with a new base.

6.2.4.2.5 Presintering and Final Firing

The fired extruded tubes were inspected for roundness, concentricity and cut to the appropriate lengths in preparation for the bisque (presintering) firing process. Tubes were prepared for hang firing. Initially, a concentric dry-pressed stabilized zirconia ring, was attached by slipping it on one end and "glueing" it to the tubes with slurry made from the same powder $[(ZrO_2)_{.85}(CaO)_{.15}]$ used in the fabrication of the extruded tubes.

Figures 6.45 and 6.46 show the arrangement of the tubes hanging between the refractory brick supports after the firing process in the Harrop kiln. The bisque firing temperature ranged from 1300-1400°C and the firing time at the maximum temperature was one hour.

Figure 6.47 shows another arrangement of vertically suspending tubes on zirconia refractory. This method is not as flexible as the brick arrangement because of the circular geometry. Furnace size limits the length of tubes that can be fired in the Harrop kiln to 16 inches. Figures 6.48 and 6.49 show the bisque fired tubes before and after cutting to length.

The final firing of the porous support tubes was done in a gas pot furnace at 1800°-1900°C for two hours. Figures 6.50 and 6.51 show the furnace arrangement during one of the firing runs. Optical pyrometers are used as sensors to chart track the temperature during the firing process with periodic corrections made with a hand-held optical pyrometer.

Fig. 6.43. Extruder parts showing different spider-core pin assemblies. Die base was modified to improve stability during extrusion.

Fig. 6.44. Extruder parts modified to handle a large material batch per extrusion.

Fig. 6.45. Samples after bisque firing in the Harrop kiln. Tubes are suspended between refractory bricks during firing.

Fig. 6.46. Overall view of bisque fired samples in the Harrop kiln.

Fig. 6.47. Early method used to "hand fire" tubing in the Harrop kiln for bisque firing.

Fig. 6.48. Extruded tubing after bisque firing.

Fig. 6.49. Bisque fired tubing cut into 6 inch lengths prior to final firing.

Fig. 6.50. Overall view of gas pot furnace during firing of support tubes. Optical pyrometer sensor is connected to temperature recorder during firing run.

Fig. 6.51. Close up of gas pot furnace during final firing of support tubes.

Figures 6.52, 6.53, 6.54 and 6.55 show the sequential views of the furnace parts as the furnace is opened, after firing, to retrieve the samples. Sample length is limited to 6 inches in this type of pot furnace. Figure 6.56 shows fired tubes.

6.2.5.2.6 Results and Discussion

Fabrication of thin wall ($\sim 1000\ \mu\text{m}$) porous tubes from loose particulate matter, such as powders of calcia-stabilized zirconia, starts with a forming process^(25,26,27,28) that leads to green bodies of sufficient 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 porous ceramic structures.

Tubes formed from a 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-additions.⁽²⁹⁾

The combustion 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.

Higher temperature calcined, calcia-stabilized zirconia materials resulted in better dimensional reproducibility of extruded porous support of the batch mix of loose powder particles, plasticizers, water and a dough-like consistence that was convenient and easy to extrude into thin wall tubing of sufficient green strength.

The inherent brittleness of calcia-stabilized zirconia tubes makes it difficult to obtain reliable strength data. Table 6.5 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^(30,31) 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

Fig. 6.52. Close up of port furnace showing refractory cover with optical pyrometer sight holes.

Fig. 6.53. Sample configuration and arrangement during final firing of support tubes.

Fig. 6.54. View showing method of loading and unloading samples into pot furnace.

Fig. 6.55. Furnace crucible arrangement without the sample holder. Crucible normally remains in position until it needs replacement.

Fig. 6.56. Samples after firing
in high temperature
gas furnace.
Note: Bell end used
to vertically suspend
samples during firing.

TABLE 6.5

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.

(Table 6.5). Table 6.6 shows the results of the flexural strength of the tubes fired at 1900°C for 2 hours. The wall thickness range was 0.042-0.047 inch, with one anomaly at 0.055 inch in the sampling group. Three levels of flexural strength were noted for this set of tubes, tested at spans of two and three inches on a three-point loading system. The scatter in the flexural strength of the samples is related to the "voids" in the tubing walls which, in turn, inflate the magnitude of the calculated percent porosity. Porosity is definitely a better criteria of flexural strength than wall thickness for this sample lot.

Information from the fuel cell fabrication group also confirmed the presence of fairly large voids in the tubing walls. The presence of large voids in the porous support tubes have resulted in cracking during the fabrication of some of the fuel cell stacks.

Thermal expansion measurements, taken on actual segments of porous support tubes, show an expansion characteristic of approximately 10×10^{-6} m/m/°C. Figure 6.57 shows the expansion and cooling curves of a porous support tube fired at 1800°C for two hours. Figures 6.58 and 6.59 are 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.

6.2.5.3 Summary

Work on the porous support tube has lead to the following:

1. Selective blending of different particle sizes of calcia-stabilized zirconia powders gives better dimensional and porosity control of extruded support tubes than material batches with additions of fugitive materials.
2. Extrusion is a process that has been proven to be amenable to the fabrication of thin wall porous support tubes. Eventually, this process can be developed into a high volume, low-cost processing system for fuel cell stacks.

TABLE 6.6

THREE-POINT FLEXURE TEST OF POROUS SUPPORT TUBES

<u>Span</u>	<u>Flexure Strength psi</u>	<u>Wall Thickness in.</u>	<u>Porosity %</u>	<u>Bulk Density g/cc</u>
2 inches	3770	0.043	31.49	3.60
	3410	0.042	31.90	3.45
	2740	0.046	33.78	3.47
	2650	0.046	33.06	3.45
	2480	0.055	31.38	3.50
	2440	0.045	37.94	3.16
	2120	0.045	35.18	3.44
	2070	0.047	34.66	3.35
3 inches	5310	0.047	32.29	3.57
	4970	0.043	29.57	3.65
	4820	0.044	31.79	3.50
	4560	0.045	30.99	3.56
	4180	0.046	33.39	3.50
	3840	0.046	33.17	3.46
	2660	0.046	42.59	3.00
	2640	0.045	32.63	3.46

Fig. 6.57—Thermal expansion of porous calcia stabilized zirconia tube-sample B-11

180 X

55 μm = 1 cm

450 X

22 μm = 1 cm

Fig 6.58 Interior Surface of Extruded Calcia-Stabilized Zirconia Tubes - In-house Development.

55 μm = 1 cm

22 μm = 1 cm

Fig 6.59 Exterior Surface of Extruded Calcia Stabilized Zirconia Tubes - In-house Development.

6.3 TASK 3. Component Testing

The purpose of this task was 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 evaluated each individual component of interest.

Thin film fuel cell components have two characteristics which make the task of electrical measurement a difficult one: they have very low electrical resistance (at operating temperature) and they are "distributed" rather than "lumped" components. For this reason attention was given to the analysis and development of special resistance measurement techniques appropriate to these components and component combinations.

A schematic of the apparatus employed for component testing is shown in Figure 6.60. Briefly, it consisted of a controlled atmosphere furnace, a specimen mounting with multiple electrical lead-ins, dual switching for current and voltage leads, a constant current source, and a digital multimeter. A more detailed description of the apparatus is given in Appendix D.

6.3.1 Subtask A. Interconnection Testing

The purpose of this task was to prepare thin film specimens of selected interconnection materials, deposited by sputtering or chemical vapor deposition, and measure their resistivity characteristics as a function of temperature and atmosphere (air, hydrogen-water). The stability of these films, under the various test conditions, was also to be evaluated.

6.3.1.1 Test Specimen with Lateral Current Flow

For maximum accuracy in determining thin film resistivities, the specimen geometry shown in Figure 6.61 was employed.

Dwg. 6406A84

Fig. 6.60 — Schematic of apparatus for measuring the electrical characteristics of simple combination specimens.

Dwg. 6414A36

Fig. 6.61. Specimen Geometry for Thin Film Interconnection Resistivity Measurement

Generally, the films were deposited by RF sputtering and ranged from 3 to 21 microns in thickness. Since an insulating substrate was employed, current flowed laterally along the film. The use of multiple electrodes effectively provided several specimens of different gauge lengths so that electrode polarization effects could be detected if important.

The most promising materials tested were based on magnesium-doped lanthanum chromite. Resistivity behavior for a specimen of this material as a function of temperature and atmosphere are shown in Figure 6.62. Reproducibility on cycling between atmospheres was found to be excellent.

It was concluded that the low resistivities and good stability observed for this material made it an excellent candidate for the interconnection material in thin film fuel cells.

6.3.1.2 Test Specimen with Current Flow Directly Through the Film

A second and much more difficult measurement of the resistivity of magnesium-doped lanthanum chromite was carried out in which the current flow was perpendicular to the plane of the film rather than parallel to it as with the previous specimen. In an actual thin film fuel cell, the current flows through the interconnection film in this manner. The resistance of the film for this geometry is very low, on the order of 6 milliohms for a 1 cm^2 area of film; consequently, any interface resistance at the contacts will become evident.

The technique devised for this type of measurement is called the crossed-electrode (CE) method, and is analagous to the crossed-bar method used for measuring metal-to-metal contact resistances. Figures 6.63 and 6.64 show the essentials of the technique. In Appendix E the ultimate limitations of the crossed-electrode (CE) method are analyzed and possibilities for further improvement discussed.

Fig. 6.62. Electrical Resistivity of $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$

Fig. 6.63— Schematic of crossed-rod method for measuring electrical contact resistance

Fig. 6.64— Schematic of crossed-electrode geometry for combination testing

A CE specimen was prepared with platinum electrodes and an 18 micron thick film of magnesium-doped lanthanum chromite. Platinum was chosen for the electrodes to permit measuring the specimen in both air and hydrogen water atmospheres. The experimental results are presented in Figure 6.65 in terms of the effective resistivity of the specimen. Qualitatively, the resistivity behavior was reassuringly similar to that obtained with lateral current flow specimens. The magnitudes of the resistivities were larger, suggesting possible interface resistance effects; however, this was not surprising, considering the very low resistance of the film being measured (31 milliohms at 1000°C).

These tests also demonstrated the viability of the CE measurement technique for studying special thin film fuel cell problems involving very low resistances.

6.3.2 Subtask 1B. Combination Testing

Combination testing involves two or more fuel cell components; consequently, interface polarizations or resistances may become evident in these measurements.

One of the most important combinations for the present fuel cell program consists of an interconnection film of doped lanthanum chromite, deposited by the EVD process on a nickel-cermet fuel electrode. In the following sections some of the testing techniques and results for this particular combination specimen are discussed.

6.3.2.1 Early Testing of Interconnection-Fuel Electrode Combination Specimens

Measurements were carried out on tubular specimens similar to that shown in Figure 6.66, consisting of a porous zirconia-calcia tube, having a nickel-zirconia cermet fuel electrode on which a 40 to 50 micron layer of strontium doped lanthanum chromite had been deposited by the EVD process. Platinum surface electrodes were applied through which the resistance of the interconnection film (plus interface resistance, if any) could be measured by a two- or three-electrode technique. Details of these techniques are given in Appendix F.

Fig. 6.65 — Effective specimen resistance vs temperature for a crossed-electrode specimen of $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$

Dwg. 64-9A23

Fig. 6.66-Tubular combination specimen with contacts for two- or three-electrode resistance measurements

Surprising results were obtained when a specimen of "strontium-doped" lanthanum chromite was tested. A plot of the resistivity vs. temperature for this combination specimen is shown in Figure 6.67. Extremely high resistivities were observed, suggesting that the strontium doping was not incorporated in the film. Subsequent chemical analysis of the film confirmed this explanation.

Successful doping of lanthanum chromite with magnesium has since been achieved, as discussed in the following section.

Fig.6.67- Resistivity vs. temperature for a tubular combination specimen (45 micron layer of $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ deposited by EVD on Ni-ZrO₂ cermet fuel electrode. Measurement in hydrogen-water atmosphere)

6.3.2.2 Recent Combination Testing of EVD-Deposited Interconnection Films

As mentioned in the previous section, the early EVD-deposited interconnection films had high resistivities due to insufficient doping. Later in the program this problem was solved, and very good doping levels of magnesium in lanthanum chromite have been achieved. Because these films are good conductors it is now possible to observe an interfacial resistance in combination specimens tested. As discussed elsewhere in this report, this is believed to originate in a thin layer on the order 2 microns thickness, formed at the very beginning of the deposition process. The resulting combination specimen consists, then, of the nickel-cermet fuel electrode, the thin interfacial resistance layer of relatively high resistivity material, and the well-doped, low resistivity interconnection film.

In the following section, a method for determining the resistivities of both layers is developed, and some experimental results based on this method are then presented.

6.3.2.2.1 Method for Determining Interconnection Film Resistivities in Combination Specimens Having Interfacial Resistance

Interfacial Resistance Absent:

If the interconnection film has no appreciable interface resistance, the current flow in a combination specimen with two platinum surface electrodes occurs as shown in Figure 6.68. Most of the current flows from electrode A directly through the film to the fuel-electrode substrate and returns in a similar manner to electrode B. Only a minute amount of current flows laterally through the film because geometrically, the resistance of this path is much higher. This can be shown schematically with the equivalent resistance network of Figure 6.70. The direct path resistance R_D is given approximately by

$$R_D = \rho \frac{\delta}{WL}$$

Fig. 6.68 — Cross-sectional view of ideal combination specimen consisting of fuel electrodes, interconnection film, and platinum electrodes for resistance measurements. Arrows indicate the current flow pattern within the I. C. film.

Fig. 6.69 — Cross-sectional view of combination specimen having an interfacial resistance layer at the fuel electrode-interconnection film boundary. Arrows indicate the current flow pattern within the I. C. and interfacial resistance layer.

Fig. 6.70 — Equivalent resistance network for combination specimens shown in the previous figure. R_L is the effective lateral resistance of the I. C. film; R_D is the effective direct resistance through the I. C. film and interfacial resistance layer, if present.

and the lateral path resistance R_L is given approximately by

$$R_L = \rho \frac{w'}{2\delta}$$

where ρ = I.C. resistivity

δ = I.C. film thickness

w = width of electrodes A and B

w' = separation between electrodes A and B

l = length of electrodes A and B

The ratio of R_L to R_D for this case is

$$\frac{R_L}{R_D} = \frac{w'w}{\delta^2}$$

For a typical specimen, $w' \sim w = 0.16$ cm and $\delta = 40 \times 10^{-4}$ cm so that

$$\frac{R_L}{R_D} \approx 1600$$

From this ratio, it is clear that R_L will have a negligible effect on resistance measured at the contacts A-B, A-N, or B-N. Any of these pairs will enable one to determine the direct resistance R_D and hence the interconnection film resistivity, ρ . In fact, it is good practice to measure all these resistances, which should obviously satisfy the relationship

$$R_{AB} = R_{AN} + R_{BN}$$

if the lateral current flow is truly small. If this relation does not hold true to within a few percent or better, it is an indication that the lateral current flow is appreciable, i.e., an interfacial resistance (or severe film resistivity gradient) is present.

Interfacial Resistance Present:

The current flow pattern in the previously discussed combination specimen now changes to that shown in Figure 6.69. An appreciable portion of the current flows laterally between contacts A and B. This is caused by the presence of the interface resistance layer which has made the direct path less favorable. To put this in quantitative terms, the lateral resistance, R_L , of the equivalent resistance network has not changed, but the direct resistance, R_D is now given by*

$$R_D \approx \rho_i \frac{\delta_i}{w\ell}$$

where δ_i and ρ_i are the interfacial layer thickness and resistivity, respectively.

Experimentally one measures the resistances R_{AB} , R_{AN} , and R_{BN} . To obtain values for R_D and R_L requires only the application of some elementary circuit theory to the network of Figure 6.70. Omitting the algebraic details one finds

$$\frac{R_L}{R_D} = \frac{1}{2 \frac{R_{AN}}{R_{AB}} - 1} \equiv r$$

and then from r

$$R_L = (1 + r/2) R_{AB}$$

$$R_D = \frac{1}{r} (1 + r/2) R_{AB}$$

In actual experiments, R_{AN} and R_{BN} may differ slightly. If so, the average of these two is used for R_{AN} in these formulas. In the previous section it was shown that for a typical specimen with no interface resistance, the ratio r (or R_L/R_D) was ~ 1600 . For practical

* It can be shown that the direct resistance of the interconnection film itself is relatively small for this case and hence is neglected here.

experimental accuracy (1%), an r of 100 probably would not be a significant indicator of appreciable interfacial resistance, while an r of 10 would be. For pronounced interface resistances r may be on the order of 1 or even less.

6.3.2.2.2 Experimental Example of a Combination Interconnection Film with Interfacial Resistance

A combination interconnection specimen was prepared, starting with the usual porous zirconia support tube covered by a nickel-cermet fuel electrode layer. On this was deposited, by the EVD process, a 40-micron thick layer of magnesium-doped lanthanum chromite. Two platinum electrodes, (1 cm x 0.17 cm x 8 microns) were then added to the chromite surface by R.F. sputtering (electrodes A, B, Figure 6.64) and the chromite film was removed at one end of the specimen to expose the nickel-cermet substrate (electrode N). After attaching suitable leads to the specimen it was placed in the measurement apparatus with a flowing hydrogen-water atmosphere. Specimen resistances R_{AB} , R_{AN} , and R_{BN} were measured over the temperature range between 60 and 1000°C. The standard precautions of polarity reversal (for cancellation of thermal e.m.f.'s) and lead resistance correction were employed. For temperatures between 400 and 1000°C, where reasonable equilibrium with the atmosphere was judged obtainable, calculated values of the ratio r (lateral resistance/direct resistance) ranged from 2.5 to 7.5, clearly indicating the presence of an interfacial resistance layer. Employing the previously developed equations, the resistances R_L and R_D were calculated and then converted to the corresponding resistivities ρ (I.C. film) and ρ_i (interfacial layer). To calculate the latter resistivity required an estimate of the thickness of the interfacial layer. This was judged to be approximately 2 microns, based on examination of specimen cross-section microphotographs and also on a knowledge of the initial transient in the EVD process.

A graph of the I.C. film and interfacial layer resistivities as a function of temperature is presented in Figure 6.71.

Fig. 6.71 — Resistivity (hydrogen-water atmosphere) vs temperature for one of the first successfully-doped, EVD-deposited interconnection films. This combination specimen consists of a 40 micron layer of magnesium-doped lanthanum chromite on a nickel-cermet fuel electrode. The significance of the interfacial resistance layer is discussed in the text.

6.3.2.3 Summary

- 1) Sputtered thin films of $\text{La}_{0.95}\text{Mg}_{0.05}\text{Cr}_{0.75}\text{Al}_{0.25}\text{O}_3$ were found to have 1000°C resistivities of approximately 0.3 Ω cm in air and 3 Ω cm in water-hydrogen ($\text{Po}_2 \sim 5 \times 10^{-16}$ atm). These values are very satisfactory for thin film fuel cell applications.
- 2) Sputtered magnesium-doped lanthanum chromite films showed stable, reversible resistivity behavior at high temperatures in equilibrium with either air or hydrogen-water atmospheres.
- 3) Electrical resistance measurements directly through a thin film of sputtered magnesium-doped lanthanum chromite showed only moderate contact resistance, indicating that there was no inherent source of layer-type resistance within the film itself, such as a second phase at the surface or cracking parallel to the plane of the film.
- 4) Resistance measurements on a combination specimen of magnesium-doped lanthanum chromite, deposited by the EVD process on a nickel-cermet fuel electrode, indicated that the bulk of the film had a resistivity of 2 Ω cm at 1000°C in a hydrogen-water atmosphere. The measurements also indicated that a very thin layer of high resistivity material was present at the interface in the initially-produced (by EVD) interconnection film.
- 5) Three special techniques for measuring electrical resistance parameters in single or combination thin film specimens were developed and tested.

6.3.3 Subtask B2. Fuel Cell Stack Fabrication and Testing

The major effort in this subtask, relating to combination testing, dealt with the actual fabrication of fuel cells in a 5 cell, series stack arrangement. The fabricated fuel cell stack was then used both to evaluate unit cell performance, as well as performance of life obtained on 3 and 5 series cells of the stack. To maintain a cohesive narrative, both the fabrication and the test performance and evaluation of the fuel cell and stack are related in this section.

6.3.3.1 Introduction

There is a great variety of methods that can be used to arrive at a fuel cell stack structure, according to the schematic in Figure 4.3, or, more realistically, Figure 6.72. Processing steps and process parameters, however, have to be selected which will not alter the structural and chemical properties of individual stack components. These components must be applied sequentially, and mechanical and optical masking techniques can be used. Masking with tapes, consisting of oxide powder layers, produces clean layer edges and is used exclusively. The demasking step must be done carefully to avoid harming the fragile stack layers, especially the electrolyte and the interconnection. The fabrication sequences, described here, take these facts into consideration, but other alternate methods have been, and are under investigation, that may ultimately lead to a less complex fabrication sequence.

6.3.3.2 Fabrication of Fuel Cell Stack Number 1

The composition and properties of the porous support tube used for stack #1 (a 5 cell series stack) were as follows:

6.3.3.2.1 Porous Support Tube Characteristics:

Length: 5" (12.7 cm)
Outer diameter: 0.5" (1.27 cm)
Wall thickness: 0.05" (0.127 cm)
Open Porosity: ~20 Vol %

- 1 - Porous Support
- 2 - Cermet Fuel Electrode
- 3 - Electrolyte
- 4 - Active Air Electrode
- 5 - Air Electrode Collector

- 6 - Interconnection Layer
- 7 - Active Cell Area
- 8 - Interconnection Area
- 9 - Inter-Cell Area

Fig. 6.72 — Cross section of two interconnected fuel cells

Composition: $(\text{ZrO}_2)_{0.85}(\text{CaO})_{0.15}$

In-house extruded tube, sintered at 1800°C for 2 hours

6.3.3.2.2 Fuel Electrode Application. The tube was sanded with 240 grit SiC abrasive paper, ultrasonically cleaned and deionized water and dried. The tube was then dipped into a slurry of n-butyl acetate, containing suspended nickel oxide [N.O] and yttria-stabilized zirconia $[(\text{ZrO}_2)_{0.9}(\text{Y}_2\text{O}_3)_{0.1}]$, and the resulting oxide coating sintered and reduced, as described in section 6.2.3.2. The fuel electrode conductance was not enhanced by additional nickel plating, although this option was available, if needed (see Section 6.2.3.2 and Figure 6.32). Figure 6.73 (top) shows the appearance of the coated tube.

6.3.3.2.3 Interconnection Application. Then the tube was mounted in the EVD reactor (as shown in Figures 6.13 and 6.14) and magnesium-doped lanthanum chromite was applied over the total length of the tube, covering the exposed area of the continuous layer of the fuel electrode in a gastight fashion according to the process described in Section 6.2.1.2 (see Figure 6.73 (bottom)). The tube was masked with adhesive PVC tape bands and the interconnection material was removed by sand-blasting to expose the fuel electrode. Additional masking and sand-blasting then removed a small band of fuel electrode to create fuel electrode bands that are covered with lanthanum chromite on one side, as seen in Figure 6.74.

6.3.3.2.4 Electrolyte Application. A 2 mil thick layer of spheroidized yttria-stabilized zirconia (10-20 μm spheres) was applied by a tape-transfer technique in the active cell area over the fuel electrode. The tube was then mounted in the EVD reactor as described in Section 6.2.1.2 and electrolyte was deposited. The deposition partially incorporated the spheroidized zirconia at the base of the deposit and consolidated the rest of the spheres at the surface. Thus a porous surface structure of nearly 30 μm thickness was created over a dense electrolyte. This porous electrolyte structure constitutes one

Fig 6.73 TOP: FUEL ELECTRODE OVER POROUS
 SUPPORT TUBE
 BOTTOM: INTERCONNECTION OVER ENTIRE
 FUEL ELECTRODE

Fig 6.74

INTERCONNECTIONS (DARK, WIDE BANDS) OVER
FUEL ELECTRODES (GREY, WIDE BAND) SEPARATED
BY INTER-CELL GAPS (SMALL DARK BANDS),

component of the composite oxide air electrode as seen in Figure 6.72, region (4). The appearance of the stack tube after the electrolyte deposition is shown in Figure 6.75.

After this fabrication step, the tube is PVC-tape masked, so that the electrolyte can be removed by sandblasting over the interconnection, as seen in Figure 6.76, so as to leave a small electrolyte overlap on both interconnection layer edges (for a gastight seal).

6.3.3.2.5 Air Electrode Application. The next step is the application of a small oxide powder tape, consisting of zirconia (by tape transfer method), for masking during the chemical vapor deposition of tin doped indium oxide, see Figure 6.77. The CVD process is described in Section 6.2.4.1.3. During this process, the fuel electrode is protected from oxidation by flowing, forming gas through the inside. Figure 6.78 shows the tube after the indium oxide deposition, with the masks removed. The last step is the impregnation of the porous electrode layer with a concentrated praseodymium nitrate solution, that decomposes into PrO_{2-x} upon heating to test temperatures. This step, however, is performed shortly before testing, to prevent excessive layer penetration, if pinholes or cracks are present in a stack of cells.

6.3.3.3 Alternate Fabrication Sequence

A fuel electrode is prepared as described above and shown in Figure 6.78, after which it is etched, according to the procedure described in Section 6.2.3.2.2, into a banded structure, see Figure 6.79 (top). Next a masking tape is applied in the interconnection area and a spheroidized zirconia tape in the active cell area, see Figure 6.79 (bottom). Electrolyte is applied over this structure, see Figure 6.80. and masking is removed from the interconnection area to expose the fuel electrode, see Figure 6.81. At this point, the active cell area requires masking during the following deposition of interconnection layer, see Figure 6.82. After the deposition of magneisum-doped lanthanum chromite the stack has the appearance of Figure 6.83 (top) and after demasking Figure 6.83 (bottom). At this point, the same processing is required for the air electrode as described in the processing sequence for cell stack #1.

Fig 6.75

EVD ELECTROLYTE APPLIED OVER ENTIRE STACK STRUCTURE.

Fig 6.76
ELECTROLYTE REMOVED OVER INTERCONNECTION
BANDS BY SANDBLASTING.

Fig 6.77

OXIDE TAPE MASKING BEFORE CVD APPLICATION
OF DOPED INDIUM OXIDE.

Fig 6.78
STACK AFTER INDIUM OXIDE CVD AND DEMASKING.

Fig 6.79

TOP: FUEL ELECTRODE BANDS PRODUCED BY
BIPOLAR ELECTROCHEMICAL ETCHING.

BOTTOM: APPLICATION OF SPHEROIDIZED ZIRCONIA TAPE
(WIDE, GREY BAND) AND INTERCONNECTION
MASKING (WHITE, SMALL BAND).

Fig 6.80

EVD ELECTROLYTE APPLIED OVER
ENTIRE STACK STRUCTURE,

Fig 6.81

ELECTROLYTE MASKING TAPES REMOVED, SHOWING EXPOSED
FUEL ELECTRODE BEFORE EVD OF INTERCONNECTION MATERIAL.

Fig 6.82

MASKING OF ACTIVE CELL AREA (WHITE BAND) BEFORE
EVD OF INTERCONNECTION MATERIAL.

Fig 6.83

TOP: EVD - LANTHANUM CHROMITE LAYER OVER TOTAL STACK.
BOTTOM: DEMASKED ACTIVE CELL AREAS AND READY FOR INDIUM
OXIDE CVD.

The reason for this alternate fabrication sequence is the better process control for achieving a flawless overlap of interconnection over electrolyte, compared with the reverse case. This preference has its reasons in thermodynamic considerations of conditions existing during the EVD process, when oxide layers are affected by the halide vapors in the reactor during the first few seconds of deposition and until a dense coverage is achieved.

6.3.3.4. The Structure of Fuel Cell Stack Components

During the course of stack fabrication, a great number of samples are prepared and microscopically examined. This requires quick-mounting, cross-section, and polishing techniques as a fast feedback laboratory tool in order to plan process conditions for subsequent component deposition.

The following Figures, 6.84 through 6.89, show the actual appearance of stack structures. An idealized schematic is attached, in each case, in order to make it easier for the reader, less familiar with the subject, to reference the location of the structure in the fuel cell stack. It should be remembered, however, that the quality of polishing is not the best, yet sufficient for drawing conclusions from experiment to experiment.

6.3.3.5 Fuel Cell Stack Performance

The tube of the fabricated 5 cell stack was compressed between two alumina adapter tubes, using gold gasket seals and a spring compression mechanism, as shown in Figure 6.90. Before heating, the air electrode was impregnated with the praseodymium nitrate solution and the tube flushed with forming gas on the inside and nitrogen plus 10% oxygen on the outside, until sealing was completed at 900°C. A thermocouple (Pt/10%Rh) was attached to each end cell with a platinum wire for current, voltage and temperature measurements. The first test data were taken at 950°C, fifty degrees below the design temperature, as a precaution to avoid the gold melting, which could cause a seal leak and result in a hot spot development.

Fig 6.84

POROUS ELECTROLYTE SKELETON AS PART
OF COMPOSITE AIR ELECTRODE.

Fig 6.85

FAULT-FREE ELECTROLYTE OVERLAP
OF INTERCONNECTION BAND.

Fig 6.86

TOP: GOOD ELECTROLYTE-INTERCONNECTION OVERLAP
AT INTER-CELL GAP

BOTTOM: GOOD ELECTROLYTE-INTERCONNECTION OVERLAP
AT CELL SIDE.

Fig 6.87

TOP: CROSS-SECTION THROUGH ACTIVE CELL AREA
OF A COMPLETED STACK

BOTTOM: CROSS-SECTION THROUGH INTERCONNECTION OF
A COMPLETED STACK (POOR QUALITY OF POLISH
REVEALS THE EXISTANCE OF AN INTER-LAYER
BETWEEN FUEL ELECTRODE AND INTERCONNECTION
MATERIAL, SEE ARROW).

Fig 6.88

TOP: DENSE ELECTROLYTE OVERLAP OVER LANTHANUM
CHROMITE INTERCONNECTION (ARROWS AT INTERFACE)

BOTTOM: DENSE LANTHANUM CHROMITE OVERLAP OVER ELECTROLYTE
(ARROWS AT INTERFACE)

Fig 6.89

INTERFACE OF FUEL ELECTRODE AND INTERCONNECTION
SHOWING INTERFACE LAYER

- 1 - Porous Stack Support Tube
- 2 - Cell Band
- 3 - Alumina Adapter Tubes
- 4 - Internal Oxygen Gage and Compression Tube

- 5 - Fuel Sensing Electrode
- 6 - Oxygen Gage, Air Electrode
- 7 - Load Spring
- 8 - Gold Washer Seal
- 9 - Fuel Feed End Cap

Fig. 6.90 — Test arrangement for thin film solid oxide fuel cell stacks

Test conditions were chosen according to the proposed goal, that is, using hydrogen plus 3% water as fuel and air as the oxidant. Both reactants were used in excess, to permit every cell in the stack to operate under nearly equal conditions. Hydrogen was used as the fuel because it quickly shows the presence of leaks and cracks and because of its fast diffusion characteristic. Unacceptable levels of leakage affect the open stack voltage and stack life performance, mainly due to indium oxide reduction and loss of its role as air electrode current collector.

The program goal was the operation of a three cell stack for 300 hours, minimum, at a current density of 200 mA/cm^2 and exhibiting a terminal voltage of 80% of the expected open stack voltage. After 300 hours of operation, the stack voltage did not deteriorate more than 10% of the initial performance.

Figure 6.91 shows the V-I characteristic of the first cell stack consisting of five cells. Assuming the test goal valid for all five cells, one sees about a ten percent lower performance, indicated by the goal margins at the 200 mA/cm^2 vertical line. After 113 hours the stack was cooled and every cell contacted by a platinum wire, in order to measure each cell voltage. It was noticed then that, during cooling, indium oxide flaked off uniformly in small areas over the interconnection, leaving a grid of conducting current collector in good contact with the air. Upon reheating, the performance was slightly better and constant for the duration of the 300 hour test. After 300 hours, the temperature was raised to 980°C with only insignificant improvement in performance. Individual cell performance was measured and is shown in Figure 6.92. Also the fast resistance change, upon current interruption, was measured. This allows the separation of electrode concentration polarization from ohmic resistance losses. The plotting of the ohmic cell stack- and cell-resistance is shown in Figure 6.93 and Figure 6.94, respectively. Figure 6.92 shows, that cell #1 and 2 perform less than the last three cells, and the reason for this is then higher internal cell resistance. If only the performance at the last three cells is

Fig. 6.91—Performance of five cell stack

Fig. 6.92 — Performance of individual cells in 5 cell stack

Fig. 6.93 — Voltage loss of five cell stack due to ohmic resistance

Fig.6.94— $1 \times R$ -voltage loss of individual cells between 300 to 600 hours of continuous operation

considered, toward the proposed 3 cell project goal, one arrives at a measured V-I curve depicted in Figure 6.95. The area between the two straight lines encompasses the target goal of 80% voltage efficiency and 72% voltage efficiency (10% degradation allowed). The three cell stack characteristic was unchanged up to the termination of the test, after 700 hours of continuous operation at 200 mA/cm^2 . The test termination was involuntary and was caused by a breakdown of the house air supply, causing the air electrode current collector to be electrochemically reduced.

6.3.3.6 Summary

It has been demonstrated, that the selection of modified lanthanum chromite as interconnection material was the correct one. This confirms our initial statement, that matching thermal expansion is a crucial requirement for a complex film structure as in this case. Life and stability of performance during the 700 hour time-span demonstrates the potential of this new interconnection material for much longer life performance. The relative modest performance, as compared with an earlier 15 cell stack, is not surprising due to the fact that a totally new and complex oxide had to be fabricated and incorporated in the stack structure.

The reduced performances of cells #1 and 2 were probably due to an interface resistance, caused by a layer that is formed during the early phase of interconnection deposition as shown in Figure 6.87, 6.88, and 6.89. Also electrical measurements confirm these findings (see Section 6.3.2.2.1). Furthermore, similar effects were expected from investigations on oxygen loss from modified lanthanum chromite (see Section 6.1.2.1.).

It was mentioned in Section 6.1.2.1 that the introduction of magnesium doping introduces oxygen ion conduction in the lanthanum chromite. To a certain degree, this is required for conductivity as well as layer growth during EVD. However, this feature is undesirable at the air electrode current collector interface with the interconnection,

Fig. 6.95—Performance of a three cell stack as part of a five cell arrangement

especially when the oxygen ion conduction of doped indium oxide is lower than that of the interconnection material. Since the vapor deposited In_2O_3 has a lower oxygen ion conduction and is dense over the interconnection, a reduction of In_2O_3 occurred that was interrupted when the stack cooled down to room temperature and some In_2O_3 flaked off due to interface weakening (reduction), see Figure 6.96. The interconnection/indium oxide interface, now being porous, prevented further reduction, because the minute amount of oxygen that had to diffuse through the dense interconnection lattice (in the presence of a steep oxygen activity gradient) was then available directly from the air and was not extracted from the In_2O_3 -lattice. This explains the stabilization of performance of the stack from 113 hours, onward.

6.3.4 Useful Life Testing

The three cell stack characteristic was unchanged for the 700 hours of operations at 950-980°C in the H_2 -3% H_2O fuel mixture. The test was terminated due to an accidental loss of the air supply from the house air line, which caused an irreversible electrochemical reduction of the indium oxide current collector. However, the test time exceeded the initial 300 hours operational life test goal aimed for at the onset of the program.

6.4 Task 4. Alternate Electrolyte and Battery Designs

Work in this area consisted of:

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

Fig 6.96

INTERCONNECTION APPEARANCE AFTER 113H OF OPERATION
AND TWO COMPLETE TEMPERATURE CYCLES.

With regard to 1., liaison was maintained with personnel at Brookhaven National Laboratories, National Bureau of Standards and, later in the program, 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, occurred to insure that promising candidates, other than yttria-stabilized zirconia solid oxide electrolyte, was not overlooked.

Alternate cell and stack designs, referred to in 2., were evaluated, with respect to fabrication procedures used in fuel cell stack preparation.

7.0 Recommendations .

Specific recommendations given in this section in detail, have been incorporated into the overall presentation of Proposed Future Work (Section 8.0).

7.1 Air Electrode

The major disadvantage of the state-of-the-art composite oxide air electrode is its inherent complexity (three component structure). A major improvement would be the availability of a one component layer. This was attempted many times in the past, yet no oxide investigated, to date, exhibits all the necessary properties. These include good electronic conductivity of tin-doped indium oxide, thermal expansion matching the other fuel cell components, and the additional feature of oxygen ion mobility which yields low concentration polarization in cells. It is worthwhile, however, to attempt to alter indium sesquioxide in this direction.

Proper doping of In_2O_3 should be attempted, to raise its own oxygen conductivity over that of the interconnection material and thus be able to function even in a dense formation. Also, developments in the field of mixed, electronic-oxionic conductors should be followed closely and applied where warranted, toward obtaining an even better air electrode.

7.2 Fuel Electrode

One remaining possible shortcoming of state-of-the-art fuel electrodes is the fact, that, during sintering, nickel oxide diffuses into the stabilized zirconia of the skeleton and the porous support tube (noticeable by dark coloration of the zirconia). The effect on the stability on zirconia has yet to be investigated. A beneficial effect, however, is the expected increase in electronic conductivity of the zirconia, which benefits electrode performance. Therefore, it is necessary to investigate better sintering schemes for the fuel electrodes, to optimize their strength to performance factor.

7.3 Porous Support Tube

Further work be done in the extrusion process to optimize pore size, improve surface texture and eliminate any non-uniformity of pore distribution in the thin wall porous support tubes.

A continuous extrusion process, that eliminates disadvantages that are inherent in a batch type, stop-and-go extrusion process, should be investigated.

Extrusion and sintering experiments should be conducted on longer tubes (>1.2 m, >4 ft) to anticipate fabrication problems when larger furnaces of increased capacity are used to produce support tubes for larger stacks.

7.4 Ideal Interconnection Composition

It is recommended that stack tests be constructed and tested in which the interconnection films are applied by sputtering, which now appears to be possible. The performance of such cell stacks, that have the most ideal interconnection composition, should not have a blocking interface with the fuel electrode. The performance of such a device could be the performance standard, with which to compare stacks with EVD-fabricated interconnections.

7.5 Electrochemical Vapor Deposition (EVD) of the Interconnection

Although cells and cell stacks can perform satisfactorily with state-of-the-art solid electrolyte, improvement should be directed to deposition reactor geometry and closer process parameter control and process simplification. Deposition length over 60 cm length have not yet been attempted and might require further process adaptation.

Also, EVD process parameters need to be "fine turned" to render improved film characteristics, as doping level, conductivity and uniformity of cross-sectional film composition, as well as achievement

of greater deposition length (from 5" to 18"). It has been demonstrated that EVD is a viable method for fabrication of complex, mixed oxides and that this method shows potential for being developed into a large scale process for interconnection application.

8.0 PROPOSED FUTURE WORK

A continuation research program has been proposed that will build upon the findings of this report on the current Department of Energy program at Westinghouse⁽¹⁾ relating to the development of the high-temperature solid oxide electrolyte (HTSOE) fuel cell. It would be aimed demonstrating extended performance and life stability of thin film, HTSOE fuel cell stacks.

The fuel cell stack, a multiplicity of series-connected cells, constitutes the basic building block of this fuel cell system. These stacks would be constructed, using the component materials and their fabrication processes developed in the present program and those materials and processes that would be further optimized during the first year of this program. Extended life would be demonstrated in single cells and small cell stacks, under conditions anticipated in the operation of stacks in a total fuel cell system. Other stacks would be tested to determine power output capability and the effect of fuel/air conditions on performance. Also, the reproducibility of stacks, with respect to cell-to-cell and overall performance, would be demonstrated, with at least 10 stacks constructed and evaluated for that purpose.

During the proposed program, four milestones would be attained. For the first milestone all the five fuel cell components -- porous support tube, fuel electrode, solid electrolyte, air electrode and the interconnection -- would be specified and the fabrication sequencing and fabrication techniques would be established in a "bench mark" stack, delivering 10W of power. To attain the second milestone at least a single cell, including an interconnection, would demonstrate a minimum of 1000 hours of life at 1000°C, under more stringent conditions than for the completed program, i.e.:

- Current density of 400 mA/cm²
- Voltage stability -- No more than 10% degradation from the initial operating cell voltage in a H₂ + 3% H₂O inlet fuel mixture.

Attainment of the second milestone would show that the thin film, high-temperature fuel concept and design is viable and should show promise of further life improvement toward what is required for utility central station operation. Achieving the third milestone would require that a small fuel cell stack, having at least 20 series connected cells, demonstrate a minimum of 1000 hours of operation, under the same conditions as for the second milestone. The fourth milestone would be attained when about 10 fabricated stacks would demonstrate reproducibility in materials fabrication and uniformity in cell and stack performance. The same test conditions as described for the other milestones would be used to operate the 10W stacks.

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

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

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

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10.1 Appendix A - Electrochemical Vapor Deposition of Solid Electrolyte

This new vapor deposition concept was initially developed at Westinghouse in an earlier, in-house program, by fabricating electrolyte layers for cells that operated at a current density level of over 500 mA/cm², without unique voltage loss caused by electrolyte resistance. However many EVD process parameters and electrolyte characteristics remained to be investigated.

The present program for DOE focused on determining the growth rate of the electrolyte under process conditions used in the past. Figure A.1 shows the principle of film growth.

The film grows over a porous substrate, in the case of our fuel cell, over the nickel-cermet fuel electrode. Figure A.1 shows only an idealized porous substrate for simplicity sake. Two different phases in film growth can be observed. The first phase is characterized by the simultaneous chemical reactions,

and

that result in the formation of a mixed oxide of zirconium and yttrium in the pore vicinity. This phase comes to a conclusion when all pores are closed with reaction product. Further film growth can take place only by the movement of ions and electronic charges. Since the reaction product of phase 1 is an ionic conductor with minimal electronic conductivity, one can write the simultaneous electrochemical reactions that occur during phase 2 of film growth as follows:

and

Fig. A.1 Scheme of oxide film growth by EVD

These equations represent sum-reactions, however, intermediate reaction steps may or may not proceed. This is also the case for Equations (1) and (2). It must be expected that the reaction products of phase 1 and phase 2 differ in composition and microstructure.

Porous zirconia tubes (12 mm O.D., 1.5 mm thickness, approximately 30 vol. % porosity, open pores of 10 μm or less, calcia-stabilized zirconia) were used as substrates in the EVD. In the fabrication of solid electrolyte films by the EVD process, the delivery of zirconium and yttrium chloride into the reaction chamber is accomplished by the chlorination of yttria-stabilized zirconia with chlorine in the presence of carbon. This reaction leads to a chloride vapor mixture that has nearly the same molar ratio of yttrium-to-zirconium as expected in the solid. The reaction takes place at 1000°C to 1100°C. Electrolyte films have been grown over separate porous tubes for 15, 30, 120, 180 and 300 minutes.

Phase 1 of the EVD process is completed very early and uniformly during the run. Phase 1 reaction product grows in a relatively high oxygen activity atmosphere, as determined by the presence of water vapor (Equations 1 and 2). The oxygen activity will change drastically during completion of pore closure and further film growth takes place under a lower oxygen activity (Equations 3 and 4). It is expected, therefore, that reaction product of phase 1 exhibits a lower electronic conductivity than that of phase 2, and depending on the degree of difference, will determine the rate of film growth during phase 2. The thickness of the phase 1 layer has been determined to be 3 to 4 μm in runs made to date. Leak-tight μm films (phase 1 + phase 2) have been grown in five hours.

Therefore, our investigations show that the EVD principle of electrolyte film growth is practical and even more favorable than originally expected, in that chemical composition seems to be close to that of the source material, that linear film growth allows going to thicker films in shorter times if so desired, and that film densification

occurs during the first few minutes of film growth. This unique behavior is not found by any other known vapor deposition process, if applied to a porous substrate, and is particularly useful in the fabrication of a solid electrolyte fuel cell.

10.2 Appendix B - Analysis of EVD Films

Scanning electron microscope (SEM) pictures of lanthanum chromite films formed by the electrochemical vapor deposition process show that they are dense and adhere tenaciously, helped, perhaps, by a significant degree of penetration into the surface voids of the nickel/zirconia cermet fuel electrode.

An SEM pattern of a typical fracture cross-section of a lanthanum chromite film deposited on the fuel electrode is shown in Figure B.1.

The composition of the film formed in a very early stage of the EVD process is more difficult to control than in later stages with the present EVD reactor design. In some instances, an undesired high resistivity layer at the interface of the lanthanum chromite interconnection and the nickel cermet fuel electrode forms and can be detected by electrical resistivity measurements through and across the film. Using the EDAX (see Appendix C) attachment of the SEM to measure the elemental composition at several two-to-three micrometer positions traversing the interface layer, the part of the interconnection film near the interface with the nickel electrode was found to have a high aluminum content in some areas, while the nickel/zirconia fuel electrode was deficient in nickel in some areas. Modification of the EVD process to obtain better control of the initial stages is thus indicated.

Analysis by the Direct Imaging Mass Spectrometer (DIMA) of the magnesium content of EVD lanthanum chromite films, doped with both magnesium and aluminum, shows that the magnesium is incorporated homogeneously in the surface layers at least. It is likely that the Mg^{2+} prefers to substitute at the small Cr^{3+} sites of the perovskite crystal structure from ion size considerations. Table B.1 shows a semi-quantitative measurement by the DIMA of magnesium in two lanthanum chromite EVD films. Sample 1 values are for cell stack sections at the center and downstream of the flow in the EVD reactor. Sample 2 values are from sections equally spaced along the cell stack length. The sections are

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 B.1 Lanthanum chromite EVD film on a porous nickel-cermet fuel electrode.