**Advanced Alternate Planar Geometry
Solid Oxide Fuel Cells**

Final Report

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1.0

Executive Summary

The potential of high temperature Solid Oxide Fuel Cells as high performance, high efficiency energy conversion device is well known. Investigation of several cell designs have been undertaken by various researchers to derive the maximum performance benefit from the device while maintaining a lower cost of production to meet the commercialization cost target. The present investigation focused on the planar SOFC design which allows for the use of mature low cost production processes to be employed. A novel design concept was investigated which allows for improvements in performance through increased interface stability, and lowering of cost through enhanced structural integrity and the use of low cost metal interconnects. The new cell design consisted of a co-sintered porous/dense/porous zirconia layer with the electrode material infiltrated into the porous layers.

The two year program, conducted by a team involving Ceramtec and the Institute of Gas Technology, culminated in a multi-cell stack test that exhibited high performance. Considerable progress was achieved in the selection of cell components, and establishing and optimizing the cell and stack fabrication parameters. It was shown that the primary stack components exhibited high conductivities and low creep at the operating temperature. The inter-cell resistive losses were shown to be small through out-of-cell characterization. The primary source of performance loss was identified to be the anode electrolyte interface. This loss however can be minimized by improving the anode infiltration technique. Manifolding and sealing of the planar devices posed considerable challenge. Even though the open circuit voltage was 250 mV/cell lower than theoretical, the two cell stack had a performance of 300 mA/cm² at 0.4V/cell with an area specific resistance of 1 Ω -cm²/cell. Improvements in manifolding are expected to provide much higher performance.

2.0

Introduction

Although Nernst is credited with discovering, in the early 1900's, that certain solid ionic oxides conduct via an oxygen ion diffusion mechanism, it was not until the late 1950's that Ruka and Weissbart at Westinghouse Electric conceived the idea that stabilized zirconia could serve as an electrolyte for a high temperature (~1000°C) solid oxide fuel cell. Since that time, Westinghouse has continued research and development of this system under sponsorship of various Federal agencies as well as through its own internal funding. As a result, Westinghouse has established itself as the leading developer of this system. Other program participants have been Institute of Gas Technology (IGT) in the early 1960's and Montana Energy Research and Development Institute in the early 1980's. Both evaluated the feasibility of constructing and testing planar cell configurations. More recently, Ztek Corporation has developed a planar cell configuration with metallic cell separator that is corrugated to allow gas access to the flat electrodes and electrolyte. One key factor claimed is that the cell package is heated to operating temperature before the holding force is applied to achieve bonding. This procedure is expected to accommodate the use of metallic interconnect that has a different thermal expansion than the ceramic components. Argonne National Laboratories (ANL) and Brookhaven National Laboratories (BNL) have been active in materials and fundamental studies for the past several years. Argonne has conceived a monolithic cell design concept that has the potential for achieving significant increase in power density because of its unique close packed cell design. Argonne and Garrett have formed a team to further develop this technology and perform engineering and scale-up work. The Europeans, mainly at Battelle and Brown-Boveri, were active in both materials and cell testing during the 1960-1980 time period. Finally, the Japanese appear to have had long interest, dating back to the early 1970's, focusing on materials studies. Thus, different developers have tried different approaches to fabrication, each with its own advantages and disadvantages. The disadvantages arising chiefly due to materials incompatibilities, however, limit performance and life of SOFC components.

The inherent brittle nature of the ceramic oxide materials used, coupled with their relatively low electrical conductivity behavior, forces constraints and limitations on the design and configuration of the solid oxide fuel cell -- that is, the low conductivity dictates thin cell components and the brittle nature of the zirconia electrolyte dictates small cells. Throughout the years, various cell configurations, including the planar approach mentioned above, have been designed and tested in an attempt to best accommodate these severe constraints. These are outlined in the next section.

2.1 Review of state-of-the-art SOFC

2.1.1 Westinghouse Approach

The most success has been achieved with variations of tubular configurations. Westinghouse has designed and tested a progression of at least three tubular design configurations: the bell-and-spigot, the segmented cell, and, most recently, the Fully Bare Anode (FBA) design. The FBA concept appears to be, by far, the most desirable tubular design. Two key features are responsible for its acceptance: 1) A relatively thick, stabilized zirconia and more recently lanthanum manganite tube is used to support the thin and fragile cell components, and 2) the anode is located on the outer diameter of the tube, thus permitting realistic current removal from each cell.

The active cell components deposited (by chemical vapor deposition or electrochemical vapor deposition) on the relatively thick, support tube are both thin and relatively fragile because of their inherent brittle nature. In addition, since the components are sequentially formed or deposited during the fabrication process, a very special set of electrochemical, chemical, and mechanical parameters is required during fabrication and must be maintained during the operating lifetime of the cell. As a result of over 25 years of research and development, most of the cell components appear to have achieved these parameters in single cell test. However, problems with component cracking have been encountered when multiple-cell configurations are operated. Moreover, the cost to manufacture cell components using some combination of electrochemical vapor deposition (EVD) and chemical vapor deposition (CVD) is very high; thus, the economic goals established to reach commercial reality is difficult to achieve. As a result, economic means to fabricate cell components are required and must be developed--this is one of the primary objectives of this project.

2.1.2 Argonne National Laboratory Approach

The Argonne's approach to fabrication of monolithic fuel cells, although elegant in concept, is extremely difficult to fabricate without the formation of microcracking at the electrode/electrolyte surfaces. These problems will increase and become more severe when a multi-cell stack is built. That is, it may be nearly impossible to sinter a multiple-cell stack and achieve the varying

densification required for each cell component. For example, the electrolyte and the interconnection must achieve >94% density for permeation-free components while the electrodes must remain porous. At the temperature of co-firing process, controlled by the sinterability of LaCrO_3 interconnect material, interdiffusion of Cr and Mn between the interconnect and the cathode, the diffusion of Mn into zirconia and formation of La and Sr zirconates at the electrolyte/cathode interface are expected to be detrimental to the cell performance.

2.1.3 Ceramtec Approach

Ceramtec has been developing a planar design SOFC, under GRI sponsorship (see section 5 for a comprehensive summary). The Ceramtec planar SOFC concept, which has been under development for just about three years, has already shown considerable progress. For example, 0.003" thin, flat and up to 4" x 4" electrolytes have been fabricated. In-cell tests have demonstrated single cell performance of 500 mW/cm², and 5-cell stack performance of 150 mW/cm² using H₂/air.

2.2 Advanced Planar Design Approach

As stated above, three SOFC design concepts are presently being developed: tubular (Westinghouse), monolithic (ANL with Garrett), and planar (Ztek and Ceramtec). Westinghouse primarily uses some combination of EVD and CVD to form the cell components, ANL primarily uses tape casting, Ztek probably uses some combination of tape casting and plasma spraying, and Ceramtec uses tape casting and screen-printing. Because of the sequential and expensive fabrication steps required in the tubular concept, it will be difficult to develop into cost effective commercial product. Therefore, the monolithic and the planar designs should be considered and means to fabricate and test such designs should be emphasized. A number of inherent problems are apparent in the monolithic design due to its design and the need to co-fire the entire cell package together as mentioned above. As a result of these concerns, a planar design in which individual cell components can be fired to different temperatures which are required to reach their optimal densities is the preferred direction to follow. Furthermore, the fabrication processes used must be scaleable to mass-production rates and be capable of reaching low costs on the commercial scale. Therefore, the challenge is to develop both the design and the fabrication processes required to stack planar SOFC cells sequentially with a separator plate, an electrolyte with electrodes being the repeat unit. This approach will result in a commercially viable flat-plate stack configuration because of low-cost materials and fabrication processes combined with the ease of assembling discrete units of the cell package. Figure 1 shows that a stack of cells consists of discrete units of

- 1) Electrolyte with electrodes deposited onto the porous layers on the electrolyte, and,
- 2) Interconnector (separator plate) with bonded electrodes.

Figure 1. Planar SOFC Configuration

The concept involves co-sintering of a dense electrolyte with porous skeletal zirconia matrix into which the electrode materials are infiltrated. The interconnector trilayer consists of a thin flat plate (perovskite or high temperature alloy) bonded to flow fields made of the corresponding electrode materials.

2.2.1 Critical Issues Related to Current SOFC Technology

Among the critical problems that limit stability of performance and life of current SOFCs, the problems associated with the lamination and firing of dissimilar materials which are expected to form a stable interface are the most severe. Brittle ceramic materials are subject to microcrack formation at grain boundaries and multi-phase interfaces (e.g., ZrO_2 - electrode interfaces), which are induced by residual stresses resulting from incompatibilities in thermal expansion. These problems have been traditionally solved by tailoring the materials compositions to match the bulk thermal expansion characteristics of the central element of the SOFC, the stabilized ZrO_2 electrolyte. There are however, some limitations to this technique which are a compromise on SOFC performance and life, necessary to preserve structural integrity of the SOFC assembly. For example, any change in material stoichiometry changes thermal expansion characteristics. Furthermore, although the bulk thermal expansion of the Ni/ZrO_2 cermet can be matched to that of stabilized ZrO_2 , at the microscopic level there remains a large mismatch due to the two phase nature of the cermet.

The cathode composition ($\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$) with the best thermal expansion match to stabilized ZrO_2 is not the composition with the highest conductivity ($\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$). This then is a compromise imposed by the design and fabrication processes of current SOFC's. The problem in the case of the Ni-ZrO_2 cermet anode is more severe due to larger thermal expansion mismatch with the electrolyte. Extensive studies were carried out at Ceramtec under a DOE funded MCFC anode development program to study the stability of anodes at the operating temperature and oxygen activities. The study clearly shows that the dominant factor in successful development of anodes with a microstructure stable over the design life of 50,000 hours is the achievement of satisfactory thermodynamically stable wetting conditions. In typical fuel gas compositions, the contact angle between Ni and ZrO_2 is obtuse. Hence, the anode microstructure, and consequently performance, will undergo a constant change until an equilibrium is reached. This implies that Ni particles which lie in contiguous contact in three dimensions will ultimately coalesce together driven by the need to minimize surface free energy.

Thus, although enormous research and development work has been carried out to identify and develop candidate materials for both anode and cathode, serious fundamental problems exist that limit both performance and life of SOFC's.

2.3 Benefits of the New Approach

Ceramatec's alternate approach to fabrication of planar SOFC's offers a unique way of improving both performance and life over current SOFC designs. The advantages of the porous ZrO_2 electrode matrix layer cofired with the electrolyte layer are:

- *Increased Resistance to Fracture:* The integral electrode matrix layer contributes to the handleability and ruggedness of the electrolyte. Room temperature fracture tests show that the load to fracture increases from 0.5N for the single layer dense electrolyte membrane to 6.0N for the multilayer composite, as shown in Figure 2. This represents a twelve fold increase in the ability to take stresses. A direct consequence of this is lower failures arising from temperature imbalances occurring in actual SOFC operation. The lower failure rate will also result in lower SOFC operating costs.

- *Electrode Materials Optimized for Electrical Performance:* As stated above, previous SOFC designs necessitated seeking a compromise between electrical and thermal expansion properties of the electrode materials. The porous electrode ZrO_2 matrix allows greater flexibility in the choice of materials with better electrical properties. This can be understood from the following considerations.

Consider the schematic illustration in Figure 3 which shows the dense ZrO_2 electrolyte membrane with the sintered porous ZrO_2 electrode matrix, the pores of which are impregnated with an electrode material. At the multiphase interfaces between the electrode material and the porous ZrO_2 , it is certainly reasonable to presume that residual stresses exist due to inhomogeneities in the thermal expansion properties. These residual stresses are relieved by the formation of interfacial microcracks. The primary advantage of the composite electrode/electrolyte membrane then becomes very clear. Microcracking takes place preferentially in the porous electrode matrix layer, and further crack propagation is confined to this layer alone, due to diffusion of the energy at the crack propagation front at and around the intentional microvoids present in the porous layer. This is similar to having a three layer composite with the outer two layers having a modulus E_1 much lower than E_2 , the modulus of the dense electrolyte layer. Any cracks, then, are confined to the outer layers with the lower modulus.

The advantages of improved electrode technology are: a) high electronic conductivity compared to presently used $\text{La}(\text{Sr})\text{MnO}_3$, b) increased effective electrode/electrolyte interface due to porous, high surface area electrode matrix concept; this ensures high current densities, c) mixed electronic/ionic conduction thus lowering polarization losses at cathode/electrolyte interface, a serious problem with the current cathode material, d) chemical stability due to one of the three

Figure 2. Load to Fracture for Single and Composite Electrode/Electrolyte Membranes

- Porous Electrode Matrix Layer has microvoids which stop crack propagation
- Imparts Structural Rigidity to Thin Ceramic

Figure 3. Schematic of Electrode Matrix/Electrolyte Composite

phases being cubic ZrO_2 , e) moderate cost, due to low content of rare earth oxide phase, and f) structural/dimensional tailorability and stability, due to rigid porous ZrO_2 ceramic matrix concept.

• *Ease of Edge Sealing*: The porous electrode matrix can be impregnated with a seal material with characteristics which can be tailored to give a pliant seal at operating temperature. This pliant seal material is immobilized in the pores of the matrix structure.

2.4 Program Management

The program was conducted with Ceramtec as the prime contractor and IGT as the subcontractor. The various tasks and the organizational responsibilities are listed in Table 1. Ceramtec managed the overall effort and conducted the materials preparation and, component and unit cell fabrication. Initial qualification testing was conducted by Ceramtec. IGT supported Ceramtec in their tasks and conducted the in-cell and out-of-cell testing. As the prime contractor, Ceramtec was solely responsible for the success of the overall program. This included completion of all tasks both at Ceramtec and at IGT in a timely manner, within budget, and reporting on the technical, financial and contractual status of the program at regular defined intervals.

Ceramtec worked closely with IGT during the out-of-cell testing phase and iteratively developed the materials and processes for fabrication of the advanced alternate planar geometry SOFC concept. Ceramtec conducted Tasks 3,4, and 5 exclusively and assisted IGT in performing Tasks 1,7,8 and 10. IGT provided input for selection of high temperature alloys in Task 6. Task 9 was jointly conducted by Ceramtec and IGT as was Task 12.

TABLE 1

PROGRAM OUTLINE AND ORGANIZATIONAL RESPONSIBILITIES

Task 1.0	Cell Design Analysis.	IGT
Task 2.0	Program Liaison and Test Facility Preparation.	Ceramatec/IGT
Task 3.0	Electrolyte Development and Fabrication.	Ceramatec
Task 4.0	Edge Seal Development and Fabrication.	Ceramatec
	Subtask 4.1 Selection of Seal Materials	
	Subtask 4.2 Fabrication of Seal Joints	
Task 5.0	Electrode Development and Fabrication.	Ceramatec
	Subtask 5.1 Selection of Alternate Electrode Materials	
Task 6.0	Interconnect Development and Fabrication	Ceramatec
	Subtask 6.1 Materials Selection	
Task 7.	Out-of-Cell Tests.	Ceramatec/IGT
Task 8.	In-Cell Testing.	Ceramatec/IGT
Task 9.0	Materials and Cell Design Update/Selection	Ceramatec/IGT
Task 10.0	Component Fabrication and Assembly	Ceramatec/IGT
Task 11.0	Long-Term In-Cell Testing	IGT
Task 12.0	Reporting.	Ceramatec/IGT

3.0

Technical Progress

3.1 Introduction

The various technical tasks to complete the program successfully were coordinated between Ceramatec and IGT as outlined in the previous section. Various parallel tasks were performed that included materials and process selection, electrochemical and mechanical characterization, both at Ceramatec and at IGT. The program evolved through single cell and multicell repeat unit tests at Ceramatec to iteratively improve materials and fabrication techniques and culminated in a successful 2-cell stack test at IGT. The various tasks and the results are summarized below.

3.2 Modeling and Design

Analysis or modeling, of the SOFC was carried out under this task. Areas which are of interest are the pressure drop across the cell, electrochemical performance, and temperature distribution. This task was being carried out to support the design of the SOFC and, for that reason, has focused on pressure drop calculations.

Pressure drop across the cell is of importance in that it is intimately related to cell and manifold scale up. It is a function of channel size and shape, and therefore is important to know for the cell design. A limitation on the pressure drop may then impose limitations on the cell performance and/or thermal management, within the cell.

Creep tests and cell seal evaluations, which are described in Sections 3.4 and 3.5, yield information about strength and integrity of the seals. This, along with the pressure drop calculations, is an essential part of the design criteria.

Analysis of the pressure drop in the SOFC design was carried out under this task. Ceramatec supplied IGT with the design criteria for the planar-ribbed SOFC including the proposed geometry and material specifications, as shown in Figure 4.

Figure 4. Side View of SOFC Package

The pressure drop can be divided into two parts: 1) the pressure drop due to friction in the channel, and 2) the pressure drop due to the change in cross-sectional area from the manifold to the channel.

The pressure drop due to friction in the channels is:

$$\Delta P_f = f(\text{gas velocity, gas density, gas viscosity, channel length, channel shape})$$

The pressure drop due to contraction from the manifold to the channels is:

$$\Delta P_c = f(\text{manifold size, channel size, gas velocity, gas density})$$

The total pressure drop is then the sum of these two pressure drops. The gas velocity is a function of the cell size and electrical output. Equations for calculating frictional losses due to pressure drop can be found in the appendix.

At present, the model does not take into account the pressure losses due to changes in the direction of flow, which may take place in the manifold. For the manifolds being considered, this is expected to be negligible.

Initially, the test cell was to be 4" x 4" with 50 mil square channels. Pressure drop calculations were carried out to consider two questions: How large a cell of this configuration would give a pressure drop lower than 0.5 psi, and how small could the channels be in a 4" x 4" cell and still meet this pressure drop criteria?

The first question relates to the limitations on scale up of the design in the future. The second relates to processing constraints.

The operating envelope is shown below. Note that the oxidant flow, and thus the efficiency, depends on the amount of heat required to be carried away in this stream. For larger cells, this becomes an issue in that pressures have to be increased beyond the limits of the cell package in order to obtain flows high enough to carry off the heat.

Operating Envelope

Operating Temperature:	1000°C
Gas Manifolding:	External
Gas Flow Direction:	Cross Flow
Fuel Utilization:	85%
Fuel Composition:	Medium-Btu gasified coal
Oxidant Utilization:	(50%)
Oxidant Composition:	Air
Cell Pressure Gradient:	0.5 to 1.0 psig
Cell Output:	400 mA/cm ²

Several additional assumptions were made for this work, namely:

- Cell operation is isothermal.
- Laminar flow occurs throughout the cell.
- Low pressures will be encountered.
- Density and velocity changes are negligible.
- The ideal gas law holds.

As mentioned before, the eventual goal of this work is a commercially viable SOFC, which is most likely a 12" x 12" stack. Table 2 shows the pressure drops in various cell sizes with 0.050" square channels. If oxidant flows are low enough and a 50% gas conversion is maintained, then a 12" x 12" cell could be used. However, IGT's experience with molten carbonate fuel cells show that an oxidant gas conversion of 10% is a more reasonable assumption because the oxidant is used to remove the heat generated by the cell. Therefore, an 8" x 8" cell could possibly meet the pressure drop criteria, however, a 12" x 12" would not.

Solutions to this problem include designing seals which can withstand pressure differentials greater than 0.5 psi and/or making larger flow channels. The issue of seal design was addressed in another task of this program. In general, however, sealing of this type of cell remains a problem.

The second question, that of how small a channel size can be tolerated in a 4" x 4" cell, is answered in Figure 5. While components with smaller channels may be easier to process, they also increase the pressure drop. Square channels as small as 25 mils appear to be acceptable. Note that one benefit of the decreased channel width is a decrease in contact resistance at the base of the channels. This may become an important issue concerning cell performance.

Table 2. PRESSURE DROP FOR VARIOUS SIZE CELLS;
0.05" CHANNELS AT 400 mA/cm²

Cell Size(in)	Utilization(%)	Oxidant Pressure Drop (psi)
4	50	0.029
8	50	0.12
12	50	0.27
8	10	0.61
12	10	1.37

Figure 5. Effect of Square Channel Size on the Pressure Drop
(4" x 4" Cell operating at 400 mA/cm² and 50% oxidant efficiency)

The actual cell size used in this project was 1.75" x 1.75". Single or two cell high packages were tested. This smaller area was necessary due to processing difficulties encountered in tape casting ribbed components. The pressure drop program was run using this configuration to identify the limits on channel size and on the number of channels. The assumptions made are listed below.

- 50% oxidant utilization
- Square channel cross section
- Fuel is a medium-Btu gasified coal
- Oxidant is air
- Cell operated at 400 mA/cm²
- Cell operated at 1000°C

Three cases were run in order to acquire guidelines for cell stack development. The results of pressure drop analysis on a 1.75" x 1.75" cell show:

Case 1. Minimize the square channel size while maintaining a contact area of 50%.

The results show that with the channels as small as 15 mils (width and height) a pressure drop of 0.22 psi would be obtained on the oxidant (high flow) side of the cell. Smaller channel sizes, for example, 10 mils would result in too high a pressure drop if a 50% contact area is to be maintained.

Case 2. Maintain the same number of channels (17) as is presently used and minimize the channel size.

In this configuration a channel as small as 20 mils (width and height) could be used. The pressure drop on the oxidant side would be 0.23 psi and the contact area would be raised to 80% of the total area. A 15 mil wide channel would yield a pressure drop of 0.73 psi on the oxidant side. At present this is considered to be too high for the SOFC.

Case 3. Square, 50 mil (length and width) channels and a contact area of 50%.

This configuration would yield a very low pressure drop (0.006 psi) on the oxidant side.

3.3 Fabrication and Process Development

3.3.1 Trilayer Development

The fabrication of the trilayer electrolyte is a key factor in the development of advanced concept solid oxide fuel cells. The three layers that are co-sintered to form integral electrode matrices provide well bonded electrode/electrolyte interfaces. Such interfaces are expected to reduce polarization losses of the cell arising from interfacial resistance. The trilayers were fabricated as follows.

Stabilized zirconia with 4 m/o yttria and 4 m/o ytterbia was cast into a thin tape using an organic binder/solvent system. This tape casting slip formulation was developed previously at Ceramtec. A tape of the porous electrode matrix layer was also cast using a similar slip formulation. In both these tapes the solids loading was about 60%. Two and three layers of the porous/dense and porous/dense/porous zirconia tapes respectively were laminated together at 40° C at 100 psi. The thicknesses of the green tapes were adjusted to provide the desired final thicknesses for the various layers.

Prior tape cast technology development at Ceramtec provided a good baseline for the trilayer development. The sintered trilayers were well bonded and did not show any microstructural evidence of delamination. The processing technique employed also resulted in flat bi- and trilayers. The flatness of electrolytes is an important criterion for stacking of planar cells. Microstructural evaluations were routinely performed with each batch of electrolytes to ensure that the various layers had the desired porosities and thicknesses. Other evaluations included creep testing of bilayer and trilayer electrolytes and electrode infiltration studies. The creep tests showed that these electrolytes are essentially creep resistant. The porosity and thicknesses of the porous layers were iteratively modified based on the results of the infiltration studies. The porosity of the porous layers were successively increased, from an initial value of about 30%, to about 50% to facilitate effective infiltration. The details of these studies are described in the appropriate sections.

3.3.2 Electrode Material Selection and Application

Material Selection

(a) Electronically Conducting ZrO₂ Based Electrode Materials

Mixed oxides based on In₂O₃-SnO₂-ZrO₂ or In₂O₃-PrO_{1.83}-ZrO₂ systems have been characterized (C.W. Griffin and J.L. Bates, Amer. Cer. Soc. Bull. vol. 65, 4, 1986) with respect to their phase equilibria, electrical conduction characteristics including transference numbers, and Seebeck coefficient measurements, and the processing characteristics. Several compositions have been identified within the In₂O₃-PrO_{1.83}-ZrO₂ system which exhibit higher conductivity than La(Sr)MnO₃; typical compositions contain about 50 mol.% In₂O₃ bcc phase and fcc ZrO₂ second phase.

In the In₂O₃-PrO₂ system the choice of compositions which exhibit higher conductivity than the presently used LaMnO₃ materials is limited to those containing between 35-50 mol% bcc In₂O₃ phase. It is also desirable that the Seebeck coefficient of the electrode be positive (i.e., exhibiting "p" type conduction) for stable conductivity in the cathode gas environment. From the reported data it appears that the best choice may be the 40/10/50 mol% composition in the three phase In₂O₃-PrO_{1.83}-ZrO₂ system. The CTE of In₂O₃ bcc phase is reported to be $9.6 \times 10^{-6} / ^\circ\text{C}$

and that of the 40/12/48 composition about $10.2 \times 10^{-6} / ^\circ\text{C}$. This is a close match with that of the electrolyte which is about $10.5 \times 10^{-6} / ^\circ\text{C}$.

A batch of $\text{In}_2\text{O}_3\text{-PrO}_{1.83}\text{-ZrO}_2$ with composition 40/10/50 mole percent was synthesized. The measured thermal expansion coefficient of a sintered bar of the material was $9.6 \times 10^{-6} / ^\circ\text{C}$ in the temperature range of room temperature to 1000°C . This is lower than the current cathode material, $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$, which has a matching thermal expansion with the electrolyte. However, with the trilayer concept, the pre-bonded electrode matrix provides interface stability and therefore deviation in electrode thermal expansion can be accommodated. Thus, the main criterion for the choice of an alternate electrode material is higher conductivity.

The conductivity of a sintered bar of above composition was measured in air as a function of temperature. The standard four probe technique was used to eliminate the contribution from the Pt lead wires. The conductivity values are plotted as a function of temperature in Figure 6.

(b) Doped "p" type perovskites

Materials with the defect perovskite structure typically show semiconducting or metallic behavior, depending on their composition. Examples of these are the Sr doped LaMnO_3 cathode materials developed by Westinghouse and non-stoichiometric compounds based on the RE-Ba- MO_3 compositions where RE can be La, Y etc.; Ba can be substituted by Ca or Sr while M usually is a transition metal cation.

A series of A and B site doped ABO_3 compositions were synthesized by the Pechini process using nitrate precursor materials. The calcined powders were characterized by XRD and all compositions were indexed to have single phase hexagonal crystal structure.

The current cathode material used in fuel cells is LaMnO_3 with 10%Sr doping on the La site (LSM). The conductivity of the material at 1000°C is about 100 S/cm. The conductivity of various ABO_3 compositions were measured using the four probe technique. The results of the conductivity measurements are summarized in Figure 7. The thermal expansion coefficient of the high conductivity composition was $10.3 \times 10^{-6} / ^\circ\text{C}$.

Of the cathode materials investigated, both perovskite based and mixed conducting $\text{In}_2\text{O}_3\text{-PrO}_{1.83}\text{-ZrO}_2$, it appears that either the baseline Sr doped LaMnO_3 or doped alternate perovskite composition would be a suitable candidate for use as SOFC cathode.

Electrode Application

Infiltration of electrode materials into the porous layers with optimum pore loading is required to achieve the benefits of the trilayer concept. Different infiltration techniques were

Figure 6. Conductivity of Alternate Cathode Material

Figure 7. Conductivity of Doped Perovskite Compositions

employed to achieve proper pore loading. These include: (1) vacuum infiltration of a slurry of fine electrode powder and (2) vacuum infiltration of electrode precursors. In both techniques moderate to high temperature calcination of the electrode after each infiltration was done either to remove the organics in the slurry or to synthesize the electrodes in-situ in the porous layers. The second technique appeared to give good infiltration of electrodes. Microstructural examination revealed that the technique allowed infiltration of electrode material to the interface of the porous/dense layers. However, with low concentration of the required cations in the precursor, multiple infiltrations were necessary to achieve the proper pore loading.

Initial infiltration trials using a slurry of anode and cathode powders proved to be difficult due to the pore structure and particle size of electrode materials. Subsequently, a cathode precursor slurry was infiltrated into the porous layer and optical microscopy indicated evidence of infiltration. A cell was tested, in air, with cathode (LSM) infiltrated on both sides. The performance of the cell was monitored at 1000°C by measuring the current density as a function of applied voltage. Initial measurement at 1 V bias indicated a current density in excess of 400 mA/cm². However, the performance degraded with time. The degradation in performance may be associated with low pore loading of the porous layer, due to single infiltration, and/or sintering of fine cathode particles leading to loss of continuity.

However, the anode infiltration trials using NiO slurry were unsuccessful. This was primarily due to the microstructure of the porous layers being incompatible for anode infiltration. This primary reason was due to the low porosity of the surface layer of the porous zirconia resulting from the lamination process employed for the trilayer fabrication. An approach similar to cathode infiltration was utilized to overcome this problem. A water soluble gel with Ni cation was synthesized and infiltrated into the porous layer. Removal of surface layer containing low porosity further improved the infiltration.

In light of the difficulties associated with the microstructure of the porous layer the porosity of the layer was increased to 40% and later to 50%. With the increased porosity, the number of infiltrations required to have adequate pore filling is studied by measuring the weight change as a function of the number of infiltrations. The results are plotted in Figure 8 and 9. The results indicated that the cathode required four infiltrations and the anode needed at least five infiltrations.

As mentioned earlier, the infiltrations of the electrodes were confirmed through optical microscopy of the fractured specimen. The infiltrated electrode materials could be clearly distinguished from the porosity of the layer through the distinct color of the electrodes. However, SEM of the polished cross-sections did not show electrode material in the porous layer. A similar observation was made at IGT in the post-test cells. This may be due to low pore loading, but more significantly, the polishing action may have resulted in the pull-out of electrode particulates due to

Figure 8. Cathode Infiltration Trials

Figure 9. Anode Infiltration Trials

differences in hardness of the zirconia porous layer and the electrodes. Examination of a fractured section of the trilayer under SEM, however, provided confirmation that the electrodes were successfully infiltrated to the interface.

To test the effectiveness of infiltrations single cells were fabricated as follows. The anode and cathode materials were infiltrated into the porous layers followed by high temperature sintering to improve adhesion. The infiltrated trilayer was then sealed to zirconia tube using the glass seal material. As part of electrode evaluation, single cells with bi-layer configurations (porous/dense zirconia) were also tested. Cells with infiltrated anode or cathode with Pt as the reference electrode on the dense layer were tested. The results indicated that the cell performance was primarily limited by the anode. The performance characteristics of LSM/ZrO₂/Pt single cell is given in Figure 10. With modified precursor infiltration technique the performance was improved as evidenced from the cell test results from IGT.

Figure 10. Single Cell Performance

3.3.3 Interconnect Development

Materials Evaluation

Alternate Perovskite Material

Considerable amount of research on doped perovskite compounds has been carried out at Ceramtec since 1976 (EPRI Contract No. RP+2278-7 as well as in house R&D). Ceramtec has identified a doped perovskite composition based on the $\text{Y}_3\text{Fe}_5\text{O}_{12}$ composition, yttrium iron garnet (YIG). The conduction characteristics of these doped materials reveal an activation energy of about 0.5 eV between 25°C and 450°C, with a conductivity of $4 \times 10^{-2}(\text{ohm-cm})^{-1}$. It is expected that at 1000°C, the conductivity will be about 2-4 $(\text{ohm-cm})^{-1}$. This could be further increased by suitable doping with divalent ions which occupy the Fe^{3+} sites. This gives rise to electronic defects causing higher conductivity. Three series of doped YIG compositions were examined.

Figure 11 shows the conductivity of a series of doped YIG compositions. The conductivity shows a small activation energy of 0.024 eV indicating relatively small variation with temperature. A second series of doped compositions was also synthesized and tested for conductivity (Figure 12). The conductivity shows an activation energy of 0.56 eV. Comparison of conductivities of the two YIG compositions show that the first series exhibit a higher conductivity ($2-6 \times 10^{-2} \text{ S/cm}$) at 700°C than the second ($0.8 - 2.5 \times 10^{-2} \text{ S/cm}$). Extrapolation of the conductivity behavior suggests that the second series may have higher conductivity ($4.5 \times 10^{-2} - 2 \times 10^{-1} \text{ S/cm}$). A third series of doped YIG compositions were synthesized and characterized. The conductivity measurements were made on dense sintered pellets. These compositions showed significantly higher conductivities ($\sim 0.4 \text{ S/cm}$) at 700°C than the previous YIG compositions at the same temperature.

A sintered bar of the high conductivity YIG material was characterized for thermal expansion behavior. The coefficient of thermal expansion was determined to be $11.5 \times 10^{-6} / ^\circ\text{C}$ which is within the acceptable range of $10.5 \times 10^{-6} / ^\circ\text{C}$ (for the electrolyte and the cathode) and $12.5 - 13.0 \times 10^{-6} / ^\circ\text{C}$ for the anode cermet.

The stability of the high conductivity YIG was characterized through conductivity measurements of dense pellets in air and in fuel atmospheres. The conductivity in air at 955°C was 3 S/cm. However, the conductivity in flowing hydrogen gas at the same temperature dropped by an order of magnitude to about 0.2 S/cm. Air was reintroduced into the sample rig and the conductivity recovered to about 2 S/cm. Upon cooling the pellet was found to have cracked. The cracking of the pellet may have contributed to the lowering of conductivity values under reducing atmosphere and upon re-oxidation. The X-ray diffraction spectra of YIG pellets as sintered

Figure 11. Conductivity of YIG as a Function of Mg Dopant Level

Figure 12. Conductivity of YIG as a Function of Cr Dopant Level

and reduced in H₂ were compared. The as-sintered pellet contained a mixture of cubic and orthorhombic phases while the reduced pellet showed presence of several other peaks that have not been identified. The XRD analysis indicated that the YIG material may undergo either a phase transformation or chemical reduction in the reducing atmosphere and thus unsuitable for use as interconnects.

High Temperature Alloys

Fabrication of thin, flat ceramic structures with flow-field ribs poses very challenging problems. In order to expedite cell testing using advanced cell design and component geometry concepts, IGT supplied a discussion of possible materials which could be used for an interconnect. IGT had carried out an in-depth survey on high temperature metal alloys for use in MCFCs.

Stamped Metal Interconnect-Electrode Materials

In order for such a ribbed electrode plate to be effective in an SOFC stack, it must have dimensional stability and resist oxidation at 1000°C. The ribbed electrode plate must act as a current collector, as well as provide flow paths for fuel and oxidant gases, so that the material must remain electronically conductive. Also, it is desirable to have a ribbed electrode plate material with a coefficient of thermal expansion similar to that of the zirconia electrolyte.

A metallic ribbed electrode plate has the advantage that it can be drawn and formed into a complex geometry that will act as a rigid spacer to yield the height needed to get sufficient cross sectional area for fuel and oxidant gas flows. In addition, it will not be prone to cracking and catastrophic failure that could occur if a brittle material were utilized. The only moderately priced commercial alloys that resist oxidation at 1000°C through formation of passivating layer are silica-, alumina-, and chromia-formers. Of these three, chromia-formers have the best chance of providing sufficiently high electronic conductivity to function effectively as a current collector. A chromia-former with a sufficient nickel content is desired to provide the high temperature strength and creep resistance necessary so that the separator plate will maintain its shape satisfactorily in an operating cell.

Figure 13 shows the composition of some readily available and reasonably affordable (under \$15/lb) alloys in the nickel-iron-chromium system. Figure 14 shows the creep strength at elevated temperatures for some of the alloys while figure 15 shows that the magnitude of the thermal coefficient of expansion of these alloys is dependent on the nickel content.

The yttria-stabilized zirconia electrolyte has a thermal coefficient of expansion of approximately $10 \times 10^{-6}/^{\circ}\text{C}$. Therefore, those alloys with greater than 60% nickel are more like the zirconia electrolyte than those alloys with intermediate nickel contents (approximately 30%, see

Figure 13. Ternary Diagram for Nickel-Iron-Chromium System Phases formed at 1200°F
 From "High Temperature Alloys Hot Performance Guide," Huntington Alloys, Inc.,
 Huntington, WV 25720

Figure 14. Creep Data for Nickel-Iron-Chromium Alloys over a range of temperatures
From "High Temperature Alloys Hot Performance Guide," Huntington Alloys, Inc.,
Huntington, WV 25720

Thermal expansion (between room temperature and temperature shown) of heat-resistant alloys based on the percent nickel.

Figure 15. Thermal Expansion Coefficients of Nickel-Iron-Chromium Alloys
From "High Temperature Alloys Hot Performance Guide," Huntington Alloys, Inc.,
Huntington, WV 25720

Figure 15). An examination of Figure 14 reveals that these higher nickel alloys also possess better resistance to creep at high temperature.

Cobalt alloys also show promise for use as a ribbed electrode structure. They have lower coefficients of thermal expansion and exhibit very good creep resistance but are very expensive. Alloy 617 is a nickel-chromium-cobalt alloy with superior creep resistance, as shown in Figure 14.

Depending on the actual rate of oxidation during long term exposure and the projected operating life of a cell, the separator plate should be between 20 and 30 thousandths of an inch thick.

Alternative Interconnect Materials

Iron oxide is a readily obtained, low-cost substance which may be suitable for use as an interconnect material. Figure 16 shows the three-layered scale which is likely to form in the oxygen potential gradient across the interconnect. The thickness of these layers depend on the magnitude of the partial pressure of oxygen present in the fuel gas. Figure 17 shows that both FeO and Fe₃O₄ are highly conductive at the operating temperature (1000°C) of the SOFC. Therefore, the magnitude of the electrical resistivity of the interconnect would be determined primarily by the Fe₂O₃ layer, where the interconnect is in contact with the oxidant gas. This layer may only be a fraction of the total interconnect surface, depending on the rate of transfer of oxygen from the cathode gas through the interconnect.

Figure 16. Oxidation Mechanisms of Iron to form a three-layered scale FeO, Fe₃O₄, and Fe₂O₃ form above 570°C through diffusion steps and interfacial reactions as shown

Figure 17. Temperature Dependence of the Electrical Conductivities of Several Electronically Conducting Oxides
(Courtesy: D. Adler)

Thus, Fe_2O_3 is the electrically insulating layer in the multi-layer iron oxide scale. In the oxidizing environment of the cathode gas, the electrical conductivity of the Fe_2O_3 lattice could be enhanced by doping the cationic sub-lattice of the oxide with a lower valent cation. The results of some work which examined the electrical resistivity of iron oxide doped with Cu, Co, or Mn indicate that replacing a fraction of the iron with a lower valent cation should result in sufficient electrical conductivity to run a series of solid oxide cells at temperature (1000°C). The electrical conductivity and thermal expansion of an interconnect fabricated from such a material must be compared to those of the electrolyte matrix and electrodes which compose the remainder of the cell package.

In-cell Evaluation

Based on the above discussion on high temperature alloys, a candidate material, HTA-1 was evaluated as an alternate interconnect. Billets of HTA-1 (1.75" x 1.75" x 0.25") were machined to provide flow fields to serve as gas channels on both sides. A two cell stack was assembled with the new interconnect material. For the first trial the cathode side of the interconnect was sputtered with a thin layer of Pt to prevent oxidation of the interconnect. The electrolytes used were not of trilayer configuration, but planar electrolytes with LSM cathode and Ni/ ZrO_2 anode screen printed and fired. No seal material was used between the electrolyte and the interconnect sub-assemblies to allow for the CTE mismatch between them. The open circuit voltage thus was lower than the theoretical value due to cross leaking. The performance of the stack at 1000°C is given in Figure 18. In this test, zirconia setter plates were used to form the manifold similar to the "wedding cake" design used by Argonne National Laboratories.

The performance results were encouraging and the test showed the feasibility of metal interconnect. Oxidation of metal interconnect at the cathode (air) side is a potential problem. In a short term test the oxidation layer on the cathode side was not apparent. However, for long term operation oxidation of metal interconnect on the air side may cause significant loss in performance. To further alleviate the oxidation problem a plate of HTA-2 (3/16" thick) was obtained. This material is expected to be more oxidation resistant than HTA-1. A relatively dense layer of cathode flow field (made of doped LaMnO_3) bonded to the metallic interconnect could further reduce the oxidation problem.

To test the electrical characteristics of the oxide layer that is formed on the surface of HTA-2 interconnects a bar of the material was subjected to three thermal cycles. The bar was left at 1000°C for one week during each cycle. The bar was conductive at 1000°C during each cycle. However, the surface oxide layer was non-conductive at room temperature. The oxide layer seemed to be adhering well to the metal. This suggests that spalling of oxide layer may not

Figure 18. Performance Characteristics of a two-cell stack using Metal Interconnect

occur during cell operation. Furthermore, the oxide layer was conductive at 1000°C. This alloy composition was subsequently tested in 2-cell stacks at Ceramtec and at IGT and exhibited good performance. The test results are summarized in subsequent sections of the report.

Fabrication of Flow Fields

The advanced interconnect concept involves a metal or ceramic planar sheet sandwiched between flow fields made of electrode materials. Tape cast flow fields made of electrodes were fabricated initially with integral gas channels. Due to difficulties associated with the fabrication of tape cast flow fields with desired flow channel depth (~0.030-0.050"), initial trials were concentrated on fabrication of porous flow fields. The pressure drop across the flow channel in such a flow field would not be high due to reduced cross-sectional area of the channels. However, creep testing of a porous cathode flow field showed low creep resistance (see section 3.4). Furthermore, considerable developmental effort is required to achieve flow fields that will have the flatness and thickness tolerances required for stacking. To expedite testing of a single cell package, an alternate fabrication technique, uniaxial pressing, was employed.

Several trials were made using different binder materials with various concentrations in order to achieve handleable green parts with integral flow channels. Initial trials were unsuccessful due to poor release from the die. With appropriate binder selection and concentration the problem was reduced. Sintered pieces of the cathode and sintered, reduced pieces of the anode were found to be conductive at room temperature. However, the flow fields warped after sintering. An effort to test a single cell package using such flow fields was unsuccessful due to severe mixing of the reactant gases resulting in low OCV of 0.65 V at 800°C. Hence, for the rest of the program, flat sintered electrode billets were machined to form flow channels.

Contact iR

In a planar multicell stack assembled using pre-fabricated components, the interface between various layers must be electrically continuous to minimize cell ohmic losses. The present concept under this program, through the use of infiltrated trilayer electrodes minimizes the interfacial losses at electrolyte/electrode interfaces. However, the interconnect assembly is made of distinct layers of metal and flow fields. The Ni/ZrO₂ anode flow field/interconnect interface is not expected to cause any performance degradation since it is a metal-metal interface. The cathode flow field / interconnect interface needs to be characterized to identify and minimize the losses. Previous characterization of HTA-2 bars confirmed the thermal cycleability of the material without loss in conductivity at temperature.

Interaction studies between the HTA-2 and other high temperature alloys were conducted. Pellets of La(Sr)MnO₃ and La(Sr)Mn(Co)O₃ were placed in contact with the candidate interconnect alloys and annealed in air at 1000°C for 24 hours. The contact interfaces of the two cathode compositions were X-rayed to identify any reactant product that may cause loss of interfacial conductivity. The analysis of the XRD pattern showed that the modified La(Sr)MnO₃ did not indicate any change when contacted with both alloys tested whereas La(Sr)MnO₃ showed peaks corresponding to La₂O₃ phase.

The influence of fabrication process of interconnect trilayer on the interfacial resistance was studied. To accomplish this, several bonding inks were utilized to bond the metal interconnect and pellets of LSM and modified LSM. The test included measurement of resistance through LSM/metal/LSM as well as modified LSM/metal/LSM with several bonding aids including Pt. Multiple thermal cycles were included as part of this interface characterization study. The results indicates that the composite consisting of modified LSM had the lowest resistance with Pt bonding ink as expected. However, an alternate electrode bonding aid was identified that had comparable low resistance.

3.4 Cell Materials Characterization

3.4.1 Tests at Ceramatec

Evaluation at Ceramatec consisted of selection and qualification of various SOFC components. This included the fabrication of electrolyte trilayers, permeability and microstructural characterization, selection and infiltration of electrode materials, evaluation of seal materials, fabrication and qualification of gas flow fields and testing of cells. The following list outlines the various tests performed for each of the components.

Electrolyte Trilayers	fabrication, permeability and microstructure
Electrode Materials	selection, infiltration, electrochemical characterization
Seal Material	selection, infiltration, efficacy testing
Flow Fields	material selection, fabrication, functionality test
Interconnect	selection, evaluation, and functionality tests
Cell Testing	electrochemical evaluation, functionality tests on single and multicell packages

Fabrication and characterization of electrolyte trilayers, electrode materials, and flow field, as well as selection and qualification of interconnect material are discussed earlier in section 3.3. A brief discussion on seal material development is given below.

Edge Seal Development

Based upon Ceramatec's past experience, edge seal performance requirements have been identified. Briefly, the seal material should have the following characteristics:

- good wetting
- bonding
- good chemical compatibility
- CTE match
- glass transition temperature, T_g compatibility

The first two criteria, coupled with good microstructure (lack of recrystallization) assure hermeticity of the seal, the third and fourth criteria assures stability to fuel/oxidant gases as well as to thermal cycling and life. The last criterion assures ease of seal fabrication. In other words, the sealing operation will be effected at a temperature above the cell operating temperature, and with $T_g < 1000^\circ \text{C}$, the seal will be compliant to accommodate any irregularities in the mating surfaces.

A seal test rig was constructed at Ceramtec for evaluation of the sealing technique as well as qualification of the seal materials. In this test, a test coupon was impregnated with the seal material and sealed onto a zirconia support tube. The support tube was then mounted in the rig with the fuel gas flowing on the outside of the tube. Any leak would be detected using the zirconia oxygen sensor. The sensor was exposed to air at the inner electrode and fuel at the outer electrode if no leak exists at the seal joint. Any leak at the seal would introduce air and increases the oxygen activity at the outer electrode of the sensor which was detected using a sensitive high impedance digital voltmeter. The seal test rig was shown to have sensitivity to small fuel leaks by deliberately allowing a pin hole to form in the seal joint and monitoring the rise in the sensor potential.

An initial composition of glass, selected from prior experience in sealing zirconia ceramic materials, was mixed and homogenized in a platinum crucible at $>1250^{\circ}\text{C}$ for 16 hrs. A rod of diameter $1/8''$ was pulled from the melt and the thermal expansion measured. The results indicate that the softening point was below 1000°C . Thus at the cell operating temperature the seal will be compliant. However, below T_g , the thermal contraction was measured to be lower than that of zirconia. The lower thermal contraction coefficient (CTC) however is not considered a major problem since the glass can accommodate compressive stresses.

The evaluation and selection of the manifold seal is discussed in section 3.5.

Electrochemical Evaluation

The performance of cells critically depends on the electrochemical characteristics of the individual components. The properties of the components, in turn, depend on the choice of material, and morphology. The morphology is primarily controlled by the processing techniques. In the case of electrolyte, the microstructure (porosity of various layers), and conductivity of the dense layer were evaluated as a means of quality control. Similarly, the electrode materials, especially the cathode compositions, were tested for conductivity. The infiltration techniques were evaluated and compared using optical microscopy as the primary tool. The results of these tests are discussed in section 3.3.

In addition to materials characterization, several single cells (5 cm^2 disc cells) and repeat unit packages (14.5 cm^2 with flow fields) were tested. The single cell tests established the material selection and processing criteria for electrolyte, electrodes, and seals. The repeat unit package tests qualified, in addition to those mentioned above, the flow fields and the interconnect. Several multicell functionality tests were also performed to qualify various interconnect materials and interconnect-cell package bonding methods. For example, two different thicknesses of interconnect metal were evaluated. One was a thick ($0.125''$) machined billet and the second was a thin ($0.05''$) flexible sheet. The performances of the 2-cell stacks are given in Figures 19 and 20.

Figure 19. Performance of a Two-cell Stack with a Thick Metal Interconnect

Figure 20. Performance of a Two-cell Stack with a Thin Metal Interconnect

3.4.2 Creep Tests at IGT

Creep tests were run on the following samples: trilayer, trilayer+seal, trilayer+anode, and LSM cathode. A complete description of the test procedure is given in the section describing the creep tests on trilayer. A summary of the results is given in Table 3.

Trilayer Creep Testing

The trilayer consists of three layers of stabilized zirconia, which form the middle section of each cell repeat unit. It consists of a fully dense zirconia layer approximately 6 mils thick sandwiched between two layers of porous zirconia. Since this component will be placed under compression during operation, it is important to measure the creep strength at operating temperatures.

Creep tests were carried out at 1000°C under a 50 psi compressive load. The test was run for 74 hours when thermocouple failure shut the test down. The thermocouple was replaced and the test was resumed and ran for an additional 126 hours.

The results indicate that primary creep caused a deformation of around 0.31% and occurred within the first 24 hours of testing. The creep rate after this point appeared to be zero within the resolution of the test equipment.

Table 3. RESULTS OF CREEP TESTING OF CANDIDATE SOFC MATERIALS

<u>Material</u>	<u>Load psi</u>	<u>Time, Hours</u>	<u>Creep, %</u>	<u>Notes</u>
Trilayer*	50	200	0.31	Samples intact
Trilayer + glass seal	53	177	0.45	No. 2 broken No. 2 delaminated
Trilayer + NiO/ZrO ₂	51	200	1.69	No. 1 broken No. 2 broken No. 3 intact No. 4 cracked
LSM	42	200	23	Sample stuck together

* Trilayer is dense zirconia electrolyte with porous layers of zirconia on each face.

Experimental Procedure

The samples from Lot PC3848CFT were shaped as irregular hexagonal pieces. Because of the uneven shape, the area was measured by tracing the shape onto a piece of paper and cutting it out. This was then compared to the weight of a piece of the same paper with a known area.

The thickness of each piece (sample) was measured in seven places and averaged (See Table 4). Five samples were placed on top of each other and glued together. The stacking was required to obtain sufficient thickness to be within the resolution of the test rig. This yielded a total sample thickness of around 0.150".

This multiple piece sample stack was placed between two alumina cylinders and held under a low load. The furnace was brought up to 1000°C at 4°C/min and allowed to stabilize. A compressive load of 50 psi was then applied and held for 74 hours, cooled to room temperature then restarted and run for an additional 126 hours. Changes in the thickness of the sample stack were measured in the creep rig and recorded. After testing, the samples were removed and the thickness of each test piece was measured in seven places as was done prior to testing.

Results

For this type of material, very little creep was expected. However, this test gave an opportunity to test the apparatus and verify that this was the case. The results of thickness measurements before and after the 74 hour test showed that there was, on average, 0.31% change in thickness over the test period. It was observed that all, or nearly all, of the creep took place in the first 24 hours of testing. This type of creep is referred to as primary creep.

The plot of change in thickness versus time shown in Figure 21 indicates that the steady state creep rate, which occurred after the first 24 hours, is essentially 0, within the limit of the instrument resolution. Thus, the trilayer material will most likely not cause any problem during use in terms of deforming under load if an initial "settling in" of less than 0.5% is accommodated. The creep rate from 74 to 200 hours appeared to be zero, within the limits of resolution of the equipment. This was also indicated by the pre- and post-test thickness measurements shown in Table 4 where the change in thickness from 74 to 200 hours was essentially zero.

Trilayer + Seal Creep Tests

Creep testing was conducted on samples of trilayer which had been infiltrated on one side with glass seal material. The samples were heated to 1000°C and placed under 53 psi load for 177 hours. Two pairs were placed in the test rig with the glass sides facing each other as shown in

Figure 21. Thickness Change versus Time for Electrolyte Trilayer Material PC3848CFT
(Tested at 1000°C under 50 psi compressive load)

Table 4. RESULTS OF CREEP TESTING OF ELECTROLYTE
TRILAYER MATERIAL PC3848 CF

(Samples were measured before and after testing for 74 hours and then tested out to 200 hours at 1000°C under a 50 psi compressive load.)

No.	Pre-Test (mils)	@ 74 Hours (mils)	Change 0-74 Hours (mils)	@ 200 Hours (Mils)	Change 74-200 Hours (Mils)
1	31.9	31.7	0.2	31.6	0.1
2	32.2	32.1	0.1	32.1	0.0
3	31.1	31.0	0.1	31.0	0.0
4	31.8	31.8	0.0	31.8	0.0
5	2.6	32.4	0.1	32.4	0.0

Figure 22. The sample thickness was measured before and after testing and the results are shown in Table 5.

Figure 23 is a plot of change in position of test rig loading rod with time. The initial positive change is due to thermal expansion during heat up of the rig. The load was applied at 7 hours and the sample held at temperature for over 170 hours.

The results of the creep test showed that very little creep ($<0.5\%$) occurred during testing. Indicator readings showed that the creep occurred during the beginning of the test and that steady state creep was 0, within the resolution of the equipment. The condition of each of the samples after testing was as follows:

Sample 1. This sample was intact after testing.

Sample 2. Delamination occurred on the side containing glass seal. A photomicrograph of this sample is shown in Figure 24.

Sample 3. This sample cracked into two pieces during testing. A photomicrograph of this sample is shown in Figure 25.

Sample 4. This sample was intact after testing.

Previous testing on samples of the trilayer only, under similar conditions, had yielded intact samples with similar creep behavior ($\sim 0.3\%$), as shown in Table 4.

Trilayer + Ni-ZrO₂ Creep Testing

Samples of trilayer which had been infiltrated on one side with anode material (NiO + ZrO₂) were also tested.

The samples were heated to 1000°C and placed under a 51 psi load for over 200 hours. Two pairs were placed in the test rig with the sides containing the anode material facing each other, as shown in Figure 22, similar to the trilayer + seal samples. The sample thickness was measured before testing and the results are shown in Table 6.

Results

None of the as-processed samples were completely flat. Sample 1 was visibly cupped with the convex side coated with anode material. Figure 26 is a photograph of the four samples after testing. The condition of the samples after test is summarized below.

Sample 1. This sample had broken into several pieces. It had stuck to Sample 2 and some of the anode material NiO + Zirconia) had remained on Sample 2.

Sample 2. This sample had broken into several pieces and had stuck to Sample 1 as described above.

Figure 22. Configuration of Creep Test carried out on Trilayer Samples with Infiltrated with Electrode Material

**Table 5. RESULTS OF CREEP TEST NO. 2: ELECTROLYTE TRILAYER
WITH GLASS SEAL ON ONE SIDE**

(Avg. sample thickness as measured before and after testing at
1000°C Under 53 psi Load)

No.	Pre-Test (Mils)	Post-Test (17 Hours) (Mils)	Change (Mils)
1	32.9	32.7	0.2
2	33.0	32.9	0.1
3	32.7	32.6	0.1
4	32.8	32.6	0.2

Sample 3. This sample was intact after testing. Most of the anode material from Sample 4 remained stuck to this sample.

Sample 4. This sample had one visible crack after testing and broke apart while being separated from Sample 3.

In general, it appeared that very little anode material had been infiltrated into the porous layer. Thus, the anode layer peeled off of the trilayer when samples were separated. Samples 3 and 4 had a combined pre-test thickness of 41.4 mils. The post-test thickness was measured as 40.7 showing a 1.69% change in thickness. It is assumed that most of this creep occurred in the anode layer, since previous testing showed little (~.3%) in the trilayer alone.

Sample breakage in Sample 1 is attributed to the stresses caused by cupping. That is, tensile stresses were created by the biaxial loading created by the cupping. Sample 2 may have been broken due to the high intensity of loading in the center by the cupped No. 1 sample.

LSM Cathode Creep Testing

Samples of LSM cathode discs were also tested. The samples were slightly oversized. Due to the increase in loading area, these samples were loaded at 42 psi instead of 50 psi. Four samples were placed into the creep rig similar to the previous tests. The samples were heated to 1000°C and a 42 psi load was placed on them. The load was held for 200 hours.

Results

The samples were only about 20% dense and were difficult to handle. This porosity, of course, lowers the true cross section of the material under load. Therefore, higher density should yield lower creep rates.

Figure 23. Results of Creep Test No. 2: Electrolyte Trilayer with Glass Seal on side
(Four stacked samples at 1000°C under 53 psi load)

Figure 24. Photomicrograph of Delamination in Sample No. 2 of Creep Test No. 2 at 8X

**Figure 25. Photomicrograph of Sample No. 3 of Creep Test No. 2
Showing Crack Position at 8X**

Table 6. INITIAL THICKNESS OF TRI LAYER-ANODE SAMPLES USED IN CREEP TEST

Sample	Thickness, mils
1	20.7
2	20.1
3	20.7
4	20.7

Figure 26. Trilayer + NiO-ZrO₂ Creep Testing
(Tests carried out under 51 psi at 1000°C for 200 hrs)

Therefore, higher density should yield lower creep rates could be expected.

Figure 27 shows that the creep of these samples was significant, 23%, after 200 hours. The samples stuck together and could not be measured individually. The stack of four samples was then taken as a whole for analysis. Initial stack height was 123 mils and final stack height was 94 mils.

The creep rate was calculated to be 5.5×10^{-4} mil per hour during the period of 30 to 200 hours. It may be possible to reduce the creep rate by around one-third if the density of the LSM could be increased to 50% of theoretical.

3.5 Manifold

The cell package, as delivered to IGT from Ceramatec, consisted of the three cell components already assembled and bonded. A drawing of this package is shown in Figure 28. The cell consisted of the trilayer, anode flow field and cathode flow field. Metal interconnects were used in the first test, CTK-1 and the two cell stack test, CTK-10.

Figure 27. LSM Cathode Samples Creep Tested at 1000°C and a 42 psi Loading

Figure 28. SOFC Single Cell Package

The package then required a manifold which served the following functions.

- Delivery of fuel at the fuel inlet side of the anode flow field and removal of the spent fuel at the fuel exhaust side of the anode flow field.
- A similar arrangement for the oxidant delivery.
- Sealing of these gases from the surrounding atmosphere as well as from each other.
- Electrical connection to each end, anode and cathode, such that a considerable amount of current could be carried.
- Capable of operating at temperatures in excess of 1000°C.

Previous work has shown that all these conditions are not easily met with previous manifold designs. IGT undertook design of a new manifold, using its experience with MCFC manifolding as well as the design of high temperature test apparatus.

3.5.1 Manifold Design

The initial manifold design is referred to as HTM-1. A schematic of this manifold is shown in Figure 29. It consisted of two cylindrical end plates machined out of a three inch round disk of Inconel 600. The selection of this material was made based upon IGT's work on metallic interconnects as described in Section 3.3. A ceramic retaining ring was placed around the cell and cemented into place. This ring was made from a 2-inch long piece of alumina tubing. Cementing of the retaining ring required considerable care and proved to be quite cumbersome

The selection of materials for this cell was based upon several criteria. One of these is the compatibility of the thermal expansion during heat up. In Table 7 the coefficients of thermal expansion are listed for the different constituents of the manifold. These were intended to be matched for sealing purposes, keeping in mind that the cell package thermal expansion has to be compatible with that of zirconia,. The higher thermal expansion in the end plates was expected to cause some problems, however, this was weighed against the desirable properties of having a conductive oxide layer at high temperatures as well as forming a fairly passive oxide layer, that would resist spalling.

The HTM-1 manifold was then used to run the first 15 cm² test at IGT, denoted CTK-1. The trial cell used in this test had a crack in the anode flow field. This test also made use of two interconnect pieces placed between the flow field and the electrode flow fields.

During operation, it was noted that the temperature inside the cell was as much as 20°C hotter than the surrounding temperature. This is indicative of leakage within the cell whereby the fuel was mixed with air and burned directly. Post-test inspection showed that considerable

TOP VIEW

SIDE VIEW

Figure 29. Initial Manifold Design (HTM-1)

Table 7. THERMAL EXPANSION COEFFICIENTS FOR MANIFOLD MATERIALS

<u>Material</u>	Thermal Expansion Coefficient /°C
Seal Material No. 29	8.1
Alumina 996 Tube	8.6
Inconel 600 End Plate	16.0
Partially Stabilized Zirconia	10.0

amount of burning did occur within the cell. Signs of burning were mainly noted at the corners of the cell as well as across the top and bottom of the cell where the interconnect plates were in contact with the end plates.

It was also noted that the machined surface of the interconnect plates were still quite rough thus, they might have allowed considerable leakage to occur. Since the metal interconnect plates were unnecessary for single cell testing, they were eliminated for the remainder of such testing. The changes made for manifold HTM-2 were aimed at solving the considerable leakage problems.

In order to improve cell sealing, the single alumina retaining tube was replaced by a four piece retaining ring which allowed easier application of the cement at the four corners of the cell. This manifold design is designated as HTM-2 and is shown in Figure 30.

The HTM-2 manifold design was used for Tests CTK-2 through CTK-6. While the output of Cell CTK-2 was similar to that which had been obtained by Ceramatec on its smaller tests (234 mA/cm² at 500 mV), Cell CTK-3 had an OCV of only 100 mV. At least part of this low performance was attributed to the existence of a poor conducting glassy phase at the manifold end plate/electrode. The source of this phase was believed to be the manifold sealing material. A study into the characteristics of several candidate seal materials was carried out and is described in Section 5.3. The results of these tests lead to the selection and use of Sauereisen Cement #8 in all subsequent cell tests at IGT. This same cell configuration and cement was then used for Cells CTK-4, 5 and 6 with small improvements in cell performance being obtained in each test.

3.5.2. Seal Material Testing and Selection

One of the main components of the SOFC manifold is the seal. These are called upon to prevent gas leakage at several points within the cell, including between the fuel and oxidant chambers, which may yield fuel consumption by burning which in turn leads to poor fuel utilization.

Figure 30. SOFC Manifold HTM with a Four Piece Retaining Ring
(The design was used on cell tests CTK-2 through CTK-9)

Another seal function is to prevent fuel from coming in contact with the cathode and oxidant coming in contact with the anode. If this does occur, then reduction of the cathode and oxidation of the anode can occur. Either case can lead to the reduction of cell output by making this area of the electrode non-conducting thus lowering the active area, or by creating a small electrochemical cell which then creates a mixed potential.

The seals therefore have to meet the following criteria.

- Good adherence to all the cell and manifold materials.
- Good dielectric properties (that is, a good electrical insulator)
- Seal hermetically.
- Not react with the surrounding materials in such a way as to degrade the properties are required for the fuel cell.
- Stability over long periods of time at temperatures in excess of 1000°C in both reducing and oxidizing atmospheres.

The materials which the seal would have to adhere to are Inconel 600 or 601, Ni/ZrO₂ cermet, LSM, and alumina.

3.5.3 Mechanical Sealing

The concept of mechanical seals was considered. With the proper design a mechanical seal can be made compliant, thus allowing for differences in expansion during initial heat up. However, mechanical seals were not selected for the reasons described below.

One of the primary constraints of our manifold design was that power removal was the most important criteria. This was based on the lessons learned by Ceramtec and Argonne with earlier manifolds which made use of the "wedding cake" design.

Thus, for the IGT design two metal end plates were placed on the top and bottom of the cell. The cell was then to be placed in compression along the vertical axis or Z direction. The purpose of this was to reduce any interfacial resistance between components. It also provided a large area for power removal.

Because of this it was decided that a mechanical seal utilizing forces or movement along the vertical axis should be avoided. This left only circumferential or planar seals around the cell. The possibility of such a seal was discussed with the manufacturer of a high temperature seal which utilizes a carbon paper surrounded by metal. Their assessment of this application was that not enough force could be placed on the seal in order to accomplish good sealing. Therefore this approach was not used.

Another drawback of a mechanical seal is the constraint that several seals have to be made in each plane. These include the seal at the top and bottom of the gas entry chambers as well as at the corner of the cell. Due to the small size of the cell, this kind of seal did not seem feasible.

Cements

The use of a high temperature cement appeared to be the best choice for this manifold. Cements have the desirable properties of being compatible with the materials used, especially the zirconia-silica cements. They also can be selected so as to have a high electrical resistance. Additionally, since they conform to the substrate, they reduce the need for machine-to-fit tolerances. This was especially desirable because of the number of tests required and the limited amount of time.

None of the manufacturers consulted, however, could guarantee that their cements would yield a hermetic seal. In spite of this drawback, cements were selected as the method of manifold sealing. Several manufacturers of high temperature cements were consulted at this time. Because of their wide variety and previous experience with their cements, a series of cements from the Sauereisen Cement Company was ordered. A list of these is given in Table 8.

Initially Sauereisen No. 29 was chosen for use in the cells. This was decided on the fact that it was based on zirconium silicate and had a thermal expansion coefficient close to that of the remaining components. While this cement proved successful in cell test CTK-2, it was subsequently blamed for the poor performance of Test CTK-3. The problem encountered in Test CTK-3 was that a glassy material was found at the electrode/end plate interface.

Seal material screening tests were run on eight different seal materials. This test consisted of 1" diameter 1" thick discs of Inconel 601 and 1" discs of 99.8% pure alumina. The cements were mixed as per the instructions except for Cement No. 29. This was mixed as per instructions (80% Powder, 20% Liquid) as well as at 90-10 and 95-5 ratios. This was an attempt to lower the silica content of the resulting cement.

The cement placed between the alumina and Inconel discs was allowed to dry overnight and then placed in a furnace. The samples were then heated at 5°C per minute to 1000°C, held for 24 hours and removed from the furnace for visual inspection.

A summary of the results is given in the appendix. The results indicated that the change in powder to liquid ratio for No. 29 cements did lower the amount of silica that was leached out. However, the No. 8 sample appeared to be the best candidate in that it did not visibly leach out silica and had some adherence to the materials.

Table 8. SAUEREISEN CEMENTS PURCHASED FOR MANIFOLD DEVELOPMENT

(Note that the components are treated as trade secrets and the major components were obtained from the MSDS. Therefore, this list does not reflect all the active components.)

Type	Major Components	Thermal Expansion °C X 10 ⁶	Recommended Max. Temp. (°C)
1	Sodium Silicate	11.2	982
6	Sodium Silicate	--	1370
8	Zirconium Silicate	4.7	1426
29	Zirconium Silicate	8.28	843
DW-30	Magnesia	--	482
31	Sodium Silicate	11.3	954
75	Calcium Aluminate	14.4	1427
78	Sodium Silicate	23.4	1427
160	Sodium Silicate	19.7	1204

Thus, the No. 8 cement was chosen for use in the manifold seals for the remainder of the cell tests at IGT.

3.5.4 Interfacial Resistance Measurements

Resistance Measurements

High resistance of the cathode/end plate interface was one possible cause of the inherent poor performance of the 15 cm² cells. An out-of-cell test was performed on this system using a four-point resistance measurement rig as shown in Figure 31. The LSM sample was 0.75 inches in diameter and 20 mils thick. This was placed under a load of approximately 2 psi and heated in air at 5°C/min to 1000°C. It was held at 1000°C for several hours and then cooled to room temperature. The sample was then reheated to 1000°C and the resistance measurements taken again.

Figure 32 shows the resulting resistance, as normalized to a 14.4 cm² area cell. The resistance was 2 milliohms at 1000°C after the first heat up. Upon cooling to room temperature, the resistance of the oxide layer formed was extremely high. However, upon reheating to 1000°C, it was found that the resistance increased to 4 milliohms.

Figure 31. Configuration of the Resistance Measurement System

Figure 32. Resistance Measurements on a LSM/Current Collector Interface
(Resistance normalized to 14.4 cm²)

These results indicate that this interfacial resistance is not an inherent problem. Two to four milliohms would be a small contribution to performance degradation in these cells since they have an apparent resistance of from 500 to 700 milliohms. A good cell is still expected to have a resistance at least an order of magnitude greater than the amount measured for the interface by this test.

3.6 Cell and Stack Testing

Cell testing was carried out in IGT's high temperature fuel cell test stand which was built under this project. The test stand was built to house solid oxide fuel cells up to 4" by 4" in size and several cells in height. A picture of the test stand is shown in Figure 33.

The gas delivery system was capable of supplying fuel and oxidant at a wide range of flow rates. The piping was all stainless steel, except the delivery of gases to the cell inside the furnace. This was accomplished using 1/4" Inconel 600 tubing and fittings. The pressure of both the fuel and oxidant were monitored.

The cell was heated using a molydisilicide furnace and was controllable with a ramp and soak controller. The temperature of the furnace was maintained with a Type B thermocouple. The temperature inside the cell was monitored using a Type K thermocouple in either the fuel inlet or oxidant outlet tubing.

The electrical load was initially applied using a 10 turn variable resistor. Later, a controllable load device, HP model 6060A was utilized. The current was carried through Inconel 600 tubing connected through the top and bottom end plates. The voltage was measured across the cell using a tube connected to the bottom end plate and a wire welded to the top end plate.

3.6.1 Single Cell Testing

Nine single cell tests were performed at IGT during this contract. The results of these tests are summarized in the appendix.

CTK-1

The first cell tested at IGT was CTK-1. The manifold used was of the design denoted HTM-1, which is described in Section 5. The cell package received from Ceramatec was a single cell package that was already bonded together. The anode flow field was cracked, which, according to Ceramatec happened during the initial processing steps.

In between the end plates and the electrodes a piece of Inconel sheet was used. While this was not necessary, it was to be indicative of the applicability of a metal interconnect when more than one cell was used in a stack.

Figure 33. IGT's High Temperature Fuel Cell Test Stand

During testing, no measurable electrical performance was obtained. Upon post-test inspection it was found that a considerable amount of leakage occurred across the top and bottom of the cell between the Inconel sheets and the end plates. This was indicated by the large amount of oxide which was created and some evidence of burning.

The initial surface condition of the Inconel sheets was fairly rough. It was thought that this roughness allowed both the oxidant and fuel gases to flow into the region of the interface and burn upon mixing.

CTK-2

This cell package was similar to that tested in CTK-1. The cell had no visible cracks or flaws prior to testing. The package was placed in the same manifold end plates as CTK-1. The end plates appeared to have a useful life of several tests requiring only a minor of cleanup and remachining. As stated previously, the shell was made from four separate pieces of alumina. A nickel retaining ring was used to provide added support but the $\text{ZrO}_2/\text{SiO}_2$ seal appeared to work well enough not to need this.

During heat up, the OCV was monitored. A graph of the cell voltage versus temperature is shown in Figure 34. The cell was held at a temperature of 980°C and gas flows were modified so as to maximize cell output. The cell behavior was then monitored under a load sufficient to lower the voltage across the cell to 400 mV. It was found that at this load the cell output rose steadily from 138 mA/cm^2 to 220 mA/cm^2 over a two hour period. A polarization curve was then obtained and is shown in Figure 35. A cell area of 14.4 cm^2 , as was measured during the post-test inspection, was used to calculate this data.

A polarization curve was also obtained at both 30 and 50 hours of hot time. These curves are shown in Figure 36. At 60 hours, cell performance degraded and could not be brought back up by changing the load or gas flow rate. The cell was then cooled down in order to investigate the cause of this degradation.

Post-analysis showed that the anode had been almost fully reduced except in the seal region near cathode inlet and outlet, and for a small portion of the anode in the region around a crack in the electrolyte near the oxidant inlet. The seal along the anode appeared to perform well and was intact at the end of the test. The seal along the cathode degraded and there was some indication of discoloration of the cathode near the seal. This may be tied to the loss of performance either due to loss of active area or poisoning of the cathode from a reaction of the cathode material with the seal material.

Figure 34. OCV vs Temperature for Test CTK-2

Figure 35. Polarization Curve for Cell CTK-2 at 980°C after 28 hours Hot Time
(Low utilization using a fuel of 80 H₂/20 CO₂ and dry air as the oxidant)

**Figure 36. Polarization Curve for Cell CTK-2 at 980°C after 30 and 50 Hours Hot Time
(Low utilization using a fuel of 80 H₂/20 CO₂ and dry air as the oxidant)**

CTK-3

CTK-3 was the third cell package tested. It was the first cell with the modified LSM cathode. All other specifications were similar to the two previous cells. It was tested under similar conditions to the CTK-2. That is, it was heated at 2°C per minute to 900°C under both flowing fuel and oxidant. The fuel was a 80% H₂/20% CO₂. Flow rates were selected for a fuel utilization of 85% and oxidant utilization of 50%.

During heat up, the OCV was monitored along with temperature. The results, shown in Figure 37, indicated that the cell performance degraded after reaching a maximum of 650 mV at 375°C. After checking to see if these problems were related to gas flow or electrical connections, and finding that this was not the case, the cell was shut down.

Figure 37. Cell OCV vs Temperature for Test CTK-3

CTK-4

CTK-4 was the fourth cell package tested. It was the second cell with the modified LSM cathode, CTK-3 being the first. All other specifications were believed to be similar to CTK-1 and CTK-2.

The goals of this test included a) improvement of the contact at the interface between the electrodes and the end plates by placing a compressive load on the cell and b) using a seal material which has less tendency to release silica on to the surrounding area. The release of silica into the electrode/end plate interface was believed to be responsible for the poor performance of CTK-3.

The cell was tested under similar conditions to the three previous cells. That is, it was heated at 2°C per minute to 900°C under both flowing fuel and oxidant. The fuel was an 80% H₂/20% CO₂. Flow rates were selected for a fuel utilization of 85% and oxidant utilization of 50% at a current density of 400 mA/cm². The compressive load on the cell perpendicular to the plan of the gas flow was increased from 0.4 psi to 1.5 psi.

The cell was operated for 150 hours. Performance was poor and the highest output was 136 mA/cm² at 400 mV at 1200°C, and low fuel and oxidant utilization. The poor performance

was attributed to high cell resistance, which at one point was found to be 0.72 to 0.75 ohm. A comparison of the polarization curve for this cell to the IR-free polarization curve is shown in Figure 38.

Post-test analysis of the cell indicated the most likely cause of high cell resistance was the transformation of the Ni to NiO along the oxidant side of the cell. The thickness of the cell was increased from 0.095 to 0.121 inches at its thickest. This may have resulted in the loss of contact between the anode and the end plate where the power is removed.

CTK-5

CTK-5 was a cell package which was essentially the same as CTK-3 and CTK-4. The purpose of this test was to improve the performance of the cell by changing the manifold slightly. Sealing was done essentially the same as CTK-4. The maximum output was 55 mA/cm² at 500 mV. This is far less than the 234 mA/cm² measured for Cell CTK-2.

The poor performance was apparently due to severe oxidation of the nickel in the anode. Over 50% of the total cell area was nickel oxide. This presumably acted to lower the active area of the cell and increase the cell resistance.

The oxidation of the nickel in the anode was attributed to leakage of the manifold at the corners of the fuel intake. This allowed the oxidant to pass into the anode chamber through the edge seal and oxidize the anode.

CTK-6

The goal of this cell was to improve the seal at the corners of the manifold while avoiding silica in the region of the electrical connection at the electrode/end plate interface. The two last cells tested (CTK-4 and 5) did not have good corner seals. This was attributed to the smaller amount of seal material used for these cells than in previous cells. The evidence for poor sealing is the severe oxidation the anode which in turn causes poor performance.

Manifold Design

The manifold used was similar to the previous ones in that Inconel end plates were used along with four alumina seal retainers. Changes made to this manifold included the following:

- Use of a manifold sealing cement, Sauereisen No. 8, which had been shown to leach less silica than the previously used cements.
- Use of an organic blocking material in order to keep the cement from entering into the flow chambers. This blocking material would then be burned out during operation.
- Use of alumina felt and nickel-chrome wire as a retaining ring around the manifold.

Figure 38. Polarization Curve for Cell CTK-4 at 1000°C
(under low fuel and oxidant utilization conditions)

Cell Performance

The cell was heated at 2°C per minute up to 1000°C. A polarization curve was obtained at this temperature and is shown in Figure 39. An increase in air flow had been shown to increase electrical output of the cell for previous tests. In this case, however, the performance was lower with increased air flow.

The cell temperature was raised to 1060°C and the performance improved. Figure 40 shows a polarization curve obtained at this temperature. Attempts to go to higher temperatures resulted in degradation of performance so the cell was shut down. Hot time was approximately 50 hours.

The maximum cell performance for this system is expected to be 250 to 300 mA/cm² at 400 mV based on the performance of 5 cm² cells using similar materials. The maximum performance obtained for this cell was 122 mA/cm² at 400 mV.

**Figure 39. Polarization Curve for Cell CTK-6 at 1000°C
(Gas Utilization was Low)**

**Figure 40. Polarization Curve for Cell CTK-6 at 1060°C
(Gas Utilization was Low)**

Several possibilities exist for the cause of this lowered performance. They include high resistance at the electrode/end plate interface, possibly due to infiltration of cement into this region. There was some evidence of cement on the electrodes after testing. Another possible reason for lowered performance is that a mixed potential may exist due to poor sealing at the cell stack edge seal. This may act similar to a crack in the electrolyte. The evidence for this lies in the lowered OCV from the 1000 mV predicted (and obtained in the 5 cm² cells) to the 832 mV obtained from this cell.

Post-Test Analysis

Visual inspection of the cell after cooling to room temperature showed that the manifold was mostly intact. Some cracking occurred at the corner seals but it was considerably less than had occurred in previous cells. This corner seal is deemed important because oxidation of the anode occurred in previous cells which had poor corner seals. Oxidation of the anode is believed to be responsible for poor performance because the thicker, non-conducting oxide layer serves to push the anode away from the end plate where power is taken off. There is also a lowering of the active area due to oxidation of the nickel.

Reduction of the anode in CTK-6 was nearly complete. It is estimated that less than 5% of the anode was oxide. All of this oxide was in a thin layer at the edge of the anode corresponding to the oxidant inlet and outlet. It also was well within the edge seal area which is not active and thus is not expected to lower performance. It is also not expected that this small an area could hold the rest of the anode away from the end plate. Two of the previous tests (CTK-4 and 5) did not have good corner seals. This was attributed to the use of less seal material used for these cells than in previous cells.

It should be noted however, that CTK-6 had very good sealing of the manifold as evidenced by the fact that less than 5% of the anode was oxidized. Because good manifold sealing had been achieved, the changes to cell CTK-7 focused on improving the electrical connection of the electrodes to the end plates.

CTK-7

Manifold Design: The manifold was redesigned slightly in order to improve the electrical connection at the end plate/electrode interface. This was one of the possible causes of lower performance of several of the previous cells. Changes include the following:

- Machining a small tab at the center of the end plate and a recess of the same size in the electrodes which the tab then fits into.
- Use of a plastic, water resistant film at the end plate/electrode interface to prevent cement from entering.

Cell Performance

The cell was heated at 2°C per minute up to 1000°C. At this temperature relatively poor performance was obtained ($>50 \text{ mA/cm}^2$ at 400 mV). The cell was then heated to 1190°C. At this temperature reasonable output of $>150 \text{ mA/cm}^2$ at 400 mV was obtained and a polarization curve is shown in Figure 41.

Post Test Analysis

The manifold showed a slight amount of leakage and burning at one corner of the fuel seal. however, manifold sealing overall looked excellent. There was very good adherence of the cathode and anode to their respective end plates, presumably due to the machined tab. At room temperature there was good conductivity from the power leads to the electrodes. This indicates that the precautions taken to insure good electrical contact had been successful.

The anode was less than 5% oxidized, indicating that the manifold corner sealing was good. The edge seal for the cathode on the fuel inlet side of the cell showed signs of deterioration and the cathode appeared to have been reduced. The evidence for this is that the cathode had become powdery and fell away upon handling. While there was evidence of a small amount of the edge seal remaining on both the cathode and anode, a significant part of the seal is missing, thus allowing gas mixing to occur at these points.

The primary cause of low performance may be due to the degradation and leakage through the edge seal of the cell. Another possibility for low performance is that the resistance of the flow fields and/or the end plates is too high. Platinum leads at the electrodes were used in the next test.

CTK-8

CTK-8 utilized the manifold improvements as developed for CTK-6 and 7. These included the use of organic materials to prevent the cement from entering into the manifold flow chambers or the electrode end plate interface. The main change for CTK-8 was the connection of platinum wires to the electrodes in the cell package.

Platinum leads were introduced in order to find out if the existence of ohmic losses were responsible for the lower than expected performance of the cells previously tested at IGT.

The platinum leads were bent so as to fit tightly within the channel of the electrode flow field. One wire was then pulled through the channel in the anode flow field closest to the oxidant outlet which was not filled with edge seal cement.

The other wire was pulled through the channel in the cathode flow field closest to the fuel inlet. These were then run out of the manifold through the curve seals. They then ran out of the furnace through an alumina thermocouple sheath.

Figure 41. Polarization Curve for Cell CTK-7
(Cell Temperature was 1190°C and Gas Utilization was Low)

The cell was heated at 2°C per minute under flowing gases. The cell was then held at 950°C overnight under no load.

The gases were adjusted for optimum performance (high flow yielding a low utilization) and a polarization curve was obtained. A convention was established whereby the standard anode and cathode voltage leads were referred to as A and C respectively. The platinum leads within the anode and cathode flow fields were then referred to as A' and C' respectively.

The polarization curve shown in Figure 42 indicates a significant difference between voltage AC and A'C' at a given load. Even more interesting is the existence at a potential difference even at open circuit. It is not clear what the cause is of the OCV differences. The difference in potential at loads, may be attributable to ohmic losses either at the end plate/electrode interface within the cell itself.

The exact location of these losses was not traceable using this system because of differences in lead material. Measurement of a potential across some leads A and A' would also

Figure 42. Polarization Curve for Cell CTK-8 at 1100°C
(Low Fuel and Oxidant Utilization)

reflect the voltage created by a nichrome/ platinum thermocouple. An example of this was the presence of a measurement of -20 to -35 mV across from leads A and A'.

CTK-9

The cell package, as received from Ceramtec was similar to the previous single cell packages (CTK-1 through CTK-7) except that the anode flow field had been reduced prior to assembly of the cell package. The purpose of this was to investigate possible improvements in performance when reduction of the flow field was not carried out in the cell itself during heat up.

The manifold was essentially the same as used in cell test CTK-8. That is, two Inconel 601 end plates were used along with a four piece alumina retaining ring. The cement used was Sauereisen No. 8 and the organic blocking materials used previously were also incorporated to aid in the manifold construction.

Two platinum leads were used as had been done for cell test CTK-8. The same notation convention is used here as was used for CTK-8. Namely, the standard anode and cathode

manifold voltage leads are leads A and C respectively. The platinum leads placed in the anode and cathode flow field were designated A' and C' respectively.

Heat up was carried out at 1°C per minute under flowing fuel and oxidant. The maximum OCV for the cell was 925 mV at 572°C across leads A'C'. The maximum OCV across leads AC was 856 mV at 627°C. The cell was heated up to 880°C. An OCV of 710 mV (A to C) and 738 mV A' to C' was obtained. The maximum output of the cell at 880°C was around 10 mA/cm² at 412 mV A to C (399 mV A' to C').

At this temperature the voltages across each set of leads was fairly close. Thus, the resistance of the manifold was not a factor at this point. The OCV at this temperature was lower than usual for these cells. This indicates that there was gas crossover either at the cell edge or within the active area.

The cell was then heated up to 975°C and a polarization curve was obtained and is shown in Figure 43. The OCV was still quite low at 701 mV A to C and 721 mV A' to C'. The overall cell performance was poor with an output of 51 mA/cm² at 370 mV A to C. At this temperature the voltage across leads A and C was higher than those across A' and C'. This may suggest that gas cross-over may be occurring in the region of the platinum leads.

The resistance of the cell when heated to 1030°C was 462 milliohms.

3.6.2 Two Cell Stack Testing

During this contract a two cell stack was tested (denoted CTK-10). The performance of this stack was comparable to the best performance of a single cell stack (CTK-2) yielding a current of 300 mA/cm² at 400 mV per cell. Both of these were comparable to the best performance of a 5 cm² test run on similar components at Ceramtec.

The two cell stack was made up of two cell packages similar to those tested in CTK-2 through CTK-8. The anode was in the oxide state and was reduced during the initial heat up. No extra wiring was brought into the cell as was done with CTK-7 and CTK-8. As received, the packages showed signs of the edge seals flaking off. It was deemed necessary to re-seal these edges in order to obtain any kind of reasonable performance. In order to have a good surface to adhere to, the original seal was carefully scraped off using a sharp steel tool. The seal material was then replaced with Sauereisen Cement #8. This is a zirconia-silica cement that had been shown to be a good sealing material for the manifold (See Section 3.5).

The cell was heated up to 1000°C at 2°C per minute under open circuit condition and flow rates calculated to give 85% fuel utilization and 50% oxidant utilization at a load of 400 mA/cm². A maximum OCV of 2.0 volts occurred at a cell temperature around 480°C.

Figure 43. Polarization Curve for Cell CTK-9

At 1000°C the fuel and oxidant flows and therefore the delivery pressures were raised up to a point where the cell output appeared to be at a maximum. This was accomplished by increasing the flow (and pressure) until the cell output started to drop. Thus, by going back and forth between the oxidant and fuel a maximum electrical output was reached. The flow of the oxidant in this case was much higher than that of the fuel. Both were off the range of the flow meters and thus no reading was obtained. However, the utilization of the gases was extremely low.

A polarization curve was obtained at this point. An open circuit voltage of 1.521 volts, or 760 mV per cell was obtained. The maximum output was 123 mA/cm² at 913 mV (456 per cell). The cell was held at open circuit and under a lower gas flow for the next 72 hours. During this time the open circuit voltage improved from around 800 to 1300 mV.

The fuel and oxidant flow was then raised as before and the cell output was measured. The output was not quite as high as had been observed before (85 mA/cm² at 848 mV). The gas flow was lowered and the cell was then left under an 84 mA/cm² load for 24 hours. The cell was then heated to 1050°C. The gas flow was changed to increase the cell output and a polarization curve

was obtained at this temperature. The open circuit voltage was 1541 mV (771 per cell) and the maximum output was 138 mA/cm² at 810 mV (405 mV per cell).

The cell was then heated to 1100°C. A polarization curve was obtained and is shown in Figure 44. The maximum output was 304 mA/cm² at 799 mV (400 mV per cell). This was similar to the outputs obtained at Ceramtec in the 5 cm² tests on a cell with similar components. At this point the cell was terminated.

3.7 Summary and Critical Issues for Future Work

As a result of this two-year effort a two-cell 15 cm² stack has been successfully tested. The performance of this stack can only be considered fair, when compared with our expectations for performance. The low performance can be attributed to insufficiencies in both the manifold and the cell package.

The performance losses associated with the manifold are centered on the need for high flow rates (and therefore high pressures and low utilization). That is, we have been able to obtain performance similar to that obtained in the 5 cm² tests, but only at extremely low utilization. This may be attributed to the lack of hermetic sealing between the flow distribution chambers (corner seals) and the edge of the cell package (edge seals). Future work should be either aimed at finding improved seal materials or redesigning the cell package to improve sealing.

The other contribution to poor performance appears to lie in the cell package itself. This is evidenced by the fact that the 5 cm² tests operated at 300 mA/cm² at 400 to 500 mV.

Based on our evaluation of the 15 cm² test cells a considerable portion of the performance losses appear to be from the electrolyte. These losses may be due to the resistance of the electrolyte due to its inherent ionic conductivity and the thickness used in the cell. Also, the presence of the porous zirconia layers on either side of the electrolyte may serve to lower the actual active area and/or increase the effective electrolyte thickness.

Use of a more porous or open structure and a thinner electrolyte may be an important step in improving the overall performance of the SOFC.

**Figure 44. Polarization Curve for 2-cell Stack CTK-10 at 1100°C
(Low Fuel and Oxidant Utilization)**

4.0

Critical Issues for Planar SOFC

Planar SOFC, a relatively new design, has made significant progress in the last few years and appears to be the focus of most developmental work in Europe and Japan. Cross flow design appears to be the commonly adopted design for ease of manifolding. The present developmental program indicated two major areas that need further improvement in achieving high performance stacks. First, efficient manifolding of the cell package to achieve theoretical open circuit voltage is needed. The primary contribution to the lack of good manifolding stems from the inadequacies of the corner seal material. In a cross flow design, any weakness in the corner seal results in intermixing of the reactant gases or extremely low utilization depending on the manifold design. The second challenge this program faced was the lack of good edge seal. The seal material developed worked exceptionally well for single cells (zirconia to zirconia contact) and stacks using lanthanum chromite based ceramic interconnects as evidenced by tests conducted under our GRI program. In the design adopted in this program, however, the contacting surfaces were the zirconia electrolyte and the electrode flow fields. The glass material developed works reasonably well on the cathode although a slight reaction with the cathode material was observed. On the anode side, however, the seal was too weak to handle the stack during manifolding. This is compounded by the volume change the anode flow field undergoes during reduction in the fuel environment. The use of a ceramic seal did not completely solve the problem. Thus, the critical issue that needs to be addressed with respect to planar design is the development of efficient edge and manifold seals.

It should be noted however, that, in spite of lower OCV the performance of one single cell package (CTK-2) as well as the two-cell stack was good and the area specific resistance was of the order of $1 \Omega\text{-cm}^2$. The single cell tests showed comparable performance characteristics even though the OCV was at the theoretical limit. The difficulties associated with current collector

attachment, with minimal or no platinum, and the associated in-plane losses tend to lower the measured performance. Thus, improvements in sealing techniques, through material or design modifications, is expected to produce planar stacks of high power density capabilities.

5.0

Planar SOFC Development Review

5.1 Discussion of Planar Design under GRI funding

Ceramtec has been developing the planar SOFC technology under a GRI funded program. The primary concept is a cross flow externally manifolded design using LaCrO_3 based interconnects. Tape cast and sintered Y-doped ZrO_2 electrolytes with screen printed LaMnO_3 cathode and Ni/ZrO_2 anode are used to form the single cells. Stacks are made using the single cells and sintered interconnects. The progress made in the GRI program is outlined below.

5.1.1 Summary of Progress

Substantial progress has been made at Ceramtec during the past four years in demonstrating that planar SOFCs are a viable and favorable approach to conversion of natural gas to electricity with high-efficiency. In Phase I, the feasibility of planar cells utilizing low cost high reliability ceramic fabrication techniques was established. The overall objective of Phase II is to establish stack technology and improve stack performance by addressing and resolving critical issues related to materials and demonstrate stable performance in planar cells and stacks. In the Phase II effort, Ceramtec has significantly advanced the SOFC materials technology base by developing alternate perovskite compositions with superior materials properties for electrodes and interconnects. In-cell verification of these materials was also performed. In addition, several promising manifold concepts for multi-stack modules have been identified for trials and further development.

Major Milestones in Phase II-A

Major technical milestones achieved in Phase II-A, (1988-1989), are:

- Scale up in cell and stack component fabrication.
- Development of alternate ceramic interconnects with conductivities of about a magnitude higher in fuel gas, at 1000°C , compared to known best values in the literature.

- Testing of > 60 stacks (including 5-cell, 20-cell and 40-cell stacks, and a 200-cell module with H₂ fuel) to evaluate designs, materials and processing and fabrication parameters to obtain baseline data on cell/stack performance and durability.
- Built and tested a 10-cell stack with metal interconnects which gave about 250 mA/cm² at 0.5 V/cell.
- Demonstrated about 70 Watts output in the first build of a 200-cell module rated at 100 watt at ABB, Switzerland in December of 1989.

Manufacturing Scale Up and Systems Development

Ceramatec has supplied SOFC components and has technology ties to several key utilities and power system developers including ABB Ltd. (Switzerland), ABB-Corporate Research Heidelberg (Germany), Osaka Gas Co. Ltd. (Osaka Japan) and Sulzer. Recently, Ceramatec has signed a teaming and cooperation agreement with Sulzer, a major cogeneration systems developer (Sales of approx. \$1,000 MM per year including Cogen Systems). This cooperation is aimed at commercializing PLANAR SOFC power systems for Cogen applications by 1996. Ceramatec has also won a contract from a group of Norwegian industries (Norsk Hydro and Saga, major Gas Utilities in Europe) to develop an 3-5 kWe engineering prototype cogen system by 1993, to be installed and tested at a customer specified site. This effort is being lead by Ceramatec in conjunction with a strong, experienced and well rounded Norcell team. The team brings together all the necessary capabilities for commercialization such as:

- Stack Technology and Engineering : Ceramatec
- Systems Design, Integration and Marketing: Sulzer
- Applications Studies and Market Access: Norsk Hydro and Saga
- Basic Studies: (NG Catalyst Dev.) -Center for Industrial Research, Oslo

Materials : U.of Utah, U. of Missouri-Roll, U. of Oslo

A US systems partner is currently being sought and will be in place before 1993.

Phase II-B Progress

Phase II-B goals are to address critical issues related to:

- Interconnection : design, fabrication and scale up
- Manifold and Seals: design and materials,
- Stack bonding methodology

The highlights of the Phase II-B effort (1990-present) to date are:

- Development of advanced interconnects materials for SOFCs.
- successful fabrication of 40-cell stacks

- demonstration of high performance (45 W peak power with $1.1 \Omega\text{-cm}^2$ ASR) in a 40-cell stack.
- endurance testing of single cells to 5000 hours, a 5-cell stack to ~1800 hours, and a 40-cell stack to ~1800 hours.
- A single cell was operated with a starting performance of ~260 mA/cm² @ 0.7V for 5000 hours with 4%/1000 hrs degradation, and a single cell at 175 mA/cm² @ 0.6 V has been operating for more than 2500 hrs with a degradation of 0.5%/1000 hrs.
- Cell performance improvement to give 300 mA/cm² @ 0.5 V/cell (no lead iR correction) at fuel utilization of ~80% has been demonstrated. Conducted over 250 cell tests and 90 stack tests (5-cell short stacks) to evaluate design, material and processing variables to obtain baseline data on cell/stack performance and durability.
- Advanced manifold concepts and sealing technology for planar stacks has demonstrated a 100 fold reduction in leak rates at temperature. Different manifold concepts are currently under evaluation.
- Successful demonstration of CH₄ fueled planar SOFC stack was shown in a 100 W module

Additionally, basic studies were conducted in order to develop a fundamental understanding of cell processes including critical factors affecting cell and stack performance degradation, via performance diagnostics using state of the art impedance spectroscopy techniques, study of electrode and interdiffusion kinetics and endurance testing of cells and stacks. Based on the results obtained to date, it appears that economically viable generation of electricity, using planar SOFC technology, from natural gas is feasible.

An extension to this current phase is proposed in order to finish the development plan proposed in Phase II-B. The work will concentrate on:

- verification of the advanced materials developed for the interconnect in stack tests;
- further optimization of electrode technology.
- scaling up the cell and stack size to 4x4 inch to make an engineering assessment of performance characteristics;
- further optimization of stack bonding and manifold sealing technology, using the stack engineering analyses as a tool, and
- studying and resolving issues related to stack performance degradation and reforming of natural gas directly on the anode.

These developments are expected to yield a performance goal of: 300 mA/cm² @ 0.7 V/cell in multicell stacks at fuel utilization approaching 85%.

Conclusions

Ceramatec has significantly advanced the SOFC materials technology base by developing and evaluating advanced materials for electrodes and interconnects. In addition, several promising manifolding concepts for stacks and multi-stack modules have been identified for trials and further development. The technical work performed will help complete the assessment of the major development options. A focused development plan and commercialization strategy is evolving for PLANAR SOFCs. A proof-of-concept sub-scale 3-5 kW engineering prototype system/product verification article is being developed is expected to be ready by 1993 for "Beta" testing.

5.2 Other SOFC Technology

5.2.1 Composite Electrolyte

Lowering of operating temperatures of SOFCs have several advantages in terms of thermodynamic efficiencies through higher operating voltages, a range of available metals for interconnects and manifolds, reduction in interdiffusion leading to degradation, and lower thermal losses. Many of the well known materials that exhibit high enough oxygen ion conductivities in the temperature range of 600 - 800°C to be used as SOFC electrolytes either exhibit high electronic conductivities (as in the case of ceria) or are unstable (eg., Bi_2O_3) in presence of fuel. One way to circumvent this problem is to apply a thin coat of zirconia on the fuel side. Work is in progress under a GRI Basic Science program to study the fabrication characteristics of co-sintering such composite electrolytes.

This preliminary effort has succeeded in the development of the composite microstructure without delamination between layers or severe warpage of the composite body associated with co-sintering materials with different sintering characteristics and thermal expansion coefficients. However the ZrO_2 rich layer, in contact with the reducing fuel gas conditions, must be free of open porosity and/or the Bi_2O_3 phase. This research has pointed out the salient features of fabrication of such tailored microstructures. This concept could be developed further and benefits such as : a) high performance due to high conductivity electrolyte, b) integrated solid state system, c) ease of thermal integration with existing thermal sources due to lower operating temperatures and d) greater material stabilities due to lower operating temperatures could be realized.

5.2.2 Proton Conductors

Two Phase I SBIR/SDIO-IST programs were successfully completed in fuel cell / electrolyzer technology. In one program, a novel composite electrolyte material was investigated as a potential high conductivity lower temperature solid electrolyte. The other SBIR/SDIO-IST program is directed towards investigating composite electrolytes based on the ACeO_3 family of solid electrolytes exploiting aliovalent doping on the Ce site to enhance the conductivity. A high

proton conductivity composition was identified. An SDIO program was awarded to develop a thermoelectric power generation device based on oxygen as the working fluid and utilizing a high temperature zirconia cell and a lower temperature cell with a bismuth oxide based electrolyte. Work on SBIR programs was discontinued due to Ceramtec's growth and transition out of the small business classification.

5.2.3 Oxygen Separation Devices

In the electrochemical ceramic products area, Ceramtec has progressed significantly in identifying, selecting and developing three product areas for commercialization. These products are analytical instrumentation for oxygen monitoring, analysis and sensing, oxygen removal and delivery systems, and energy systems.

6.0

Conclusions and Recommendations

The two year investigation of the advanced design resulted in proving that the trilayer concept of cell fabrication provide high creep resistance as well as high performance. The program identified a high temperature alloy for use as interconnects that was stable with time and temperature cycles.

There are, however, two factors that limited the performance of the cells. Firstly, the design and fabrication of a manifold that will result in theoretical OCV is essential for improving the performance and the efficiency of the system. Lack of adequate edge seal, when metal interconnects with high CTE are used, exacerbate the problem. The second problem is related to poor anode performance at the anode electrolyte interface as well as poor structural integrity of the anode flow fields.

Several improvements are possible that will lead to performance enhancement. Processing improvements could lead to decrease in thickness of the dense layer and increase in the porosity of the porous layers. The thinner electrolyte reduces the internal resistance of the cell and the more open porous layer enhances the infiltration process thereby reduces the interface resistance. Modifications to improve the integrity of the anode flow field is also expected to reduce the possibility of edge seal leaks. These improvements, along with manifold improvements are expected to provide commercial scale prototype with high performance.

APPENDIX A. EQUATIONS FOR PRESSURE DROP CALCULATIONS

CHANNEL FRICTION LOSSES (Fanning Equation)

$$\Delta P_f = 4f L/D \times \rho w^2 / 2$$

Where:

ΔP	=	Pressure drop
L	=	Length of channel
D	=	Hydraulic diameter
w	=	Flow velocity
f	=	Friction factor $f(Re)$
ρ	=	Gas density

CROSS SECTION CHANGE (Weisbach Equation)

$$\Delta P_c = 1.5/2 \rho w^2$$

Where:

ΔP	=	Pressure drop
ρ	=	Gas density
w	=	Flow velocity in the channel
1.5	=	Combined friction factor

Table A-1. RESULTS OF SEAL MATERIAL SCREENING TESTS.
RUN AT 1000°C FOR 24 HOURS

Sauereisen Cement Type	Color*	Amount of Silica	Adherence	Appearance, etc.
29-Std. mixture	Al ₂ O ₃ -Green Ni-Green	Small amount on disc and Ni	Al ₂ O ₃ -- good Ni -- poor	Strong seal, corres. on Ni
29-90% Powder 10% Liquid	Al ₂ O ₂ -green Ni-green	Small amount on disc	Al ₂ O ₃ -- good	Strong seal
29-95% Powder 10% Liquid	Only under sample	Very small	Al ₂ O ₃ -- good	Cracked, possibly too much H ₂ O
1	Some yellow	Yes	Poor overall	Curled up, Separated around sample
6	Some green	Small	Al ₂ O ₃ -- good Ni -- poor	--
30	Green on Ni		Al ₂ O ₃ -- some	Seal material was very soft
31	--	Yes	--	Severe oxidation of Ni
75	None	None	Poor overall	--
78	--	None	Al ₂ O ₃ -- good Ni -- poor	Formation of a dark powder under Ni
8	Some green	None	Al ₂ O ₃ -- good	

* Yellow or green coloring appears to be related to the reactions between the Inconel and the cement. This may be indicative of the formation of a silicate and/or an oxide, say Cr₂O₃ or NiO.

Table A-2. SUMMARY OF MANIFOLD DESIGN AND TEST RESULTS

	Manifold Type	Seal	End Plate Material	T°C	mA/ cm ²	mV	Resistance mΩ	Comments
CTK-1	HTM-1	#29	1	--	--	--	--	No measurable performance noted
CTK-2	HTM-2	#29	1	1100	234	500	--	Best performance
CTK-3	HTM-2	#29	1	--	--	--	--	Silica at electrode interface caused poor conductivity
CTK-4	HTM-2	#8	2	1000	30	500	500-700	
CTK-5	HTM-2	#8	2	1000	55	500	400-600	
CTK-6	HTM-2	#8	2	1060	120	400	--	Considerable improvements in manifold construction mode
CTK-7	HTM-2	#8	2	1190	170	400	--	
CTK-8	HTM-2	#8	2	1100	108	415	--	Utilized platinum leads inside cell
CTK-9	HTM-2	#8	2	975	51	307	462	
CTK-10	HTM-3	#8	2	1109	302	804 (402/cell)	308	Two cell stack

End Plate Material 1 = inconel 600 2 = inconel 601

END

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