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Status of Molten Carbonate Fuel Cell Technology

by

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STATUS OF MOLTEN CARBONATE FUEL CELL TECHNOLOGY

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ABSTRACT

A molten carbonate fuel cell integrated with a coal gasification power plant is one of the most promising coal-using technologies because of its high efficiency, acceptable cost, and environmental acceptability. The high-temperature heat available from the fuel cell may be used in a bottoming cycle and/or industrial cogeneration applications. However, for the molten carbonate system to achieve these goals, continued developmental work is required which must take account of the operating conditions of the application. This paper discusses the progress made in improving cell performance and life and in producing inexpensive cell components. Performance is enhanced by alternate electrolytes and electrode compositions and increased pressures; life by control of contaminants, electrode-electrolyte behavior, and electrolyte loss; and cost by multicell stack designs and new means of fabricating components, the electrolyte tile, and substrate materials. The status, direction, and priority of future research and engineering efforts will also be discussed.

INTRODUCTION

Molten carbonate fuel cell research has been under way in the U.S. and at IGT for over 20 years. Because the system has been aimed primarily at the industrial and utility markets, its development has lagged behind the phosphoric acid system (first generation) which benefited from significant technical advances made during the TARGET program(1) of the '60's and the DOE-EPRI-UTC program(2) of the '70's. Interest in the molten carbonate system, sometimes called a "second generation system," began to increase during the energy crisis of the mid 1970's because of several inherent and unique characteristics which make it attractive for larger system applications where cost, fuel flexibility, and efficiency are of prime concern:

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- Cost — No noble metal electrode catalysts are required. The remaining cell components utilize readily available and cost-effective materials.

- Fuel Flexibility — Because of its elevated operating temperature any solid, liquid, or gaseous hydrocarbon can be used to form a primary feed containing H_2, CO, CO_2, and H_2O.

- Efficiency — ECAS(3) and many subsequent studies have shown total system efficiencies of 50% using coal as the hydrocarbon fuel and utilizing the available high quality fuel cell heat in a steam bottoming cycle.

A total fuel cell system contains three major subsystems — a fuel processing section, the fuel cell section, and a DC to AC inverter section. Such a system configuration for a multihundred-megawatt base-load plant is shown in Figure 1.

Recently, the range of potential application has been expanded to include much smaller gas- or oil-fired cogenerating systems wherein the high-temperature reject heat supplies all or part of the process heat requirements.(4) These systems obtain benefits not only from heat utilization but also from the fuel cell efficiency in power generation. This yields net energy savings of 35% to 50% for some major energy consuming industries (Table 1).

Table 1. EFFECT OF COGENERATION ON ENERGY SAVINGS
WITH MOLTEN CARBONATE FUEL CELL

Process	Total Energy Savings	Energy Savings Due to High Fuel Cell Efficiency	Energy Savings Due to Cogeneration
Chlorine/Caustic	49.0	19.0	30.0
Newsprint	50.0	18.5	31.5
Magnesium	46.0	18.0	28.0
LDPE	36.0	16.5	19.5
Carbon-Steel Castings	34.0	14.0	20.0
Copper	45.5	12.0	33.5
Cement	8.0	3.0	5.0
Aluminum Fabrication	37.7	8.5	29.2

This paper will review the status and direction of present research at IGT and, where pertinent, efforts of General Electric Corp. (GE) with whom we are participating in a major, DOE-funded commercialization effort. The performance goals which are believed necessary to assure a substantial penetration in the central station market are given in Table 2. The goals for cogeneration systems, especially as regards thermal cycles and cost, have not been adequately defined. A summary of the present technology status is shown in Tables 3 and 4. Comparing the present status to the goals shown in Table 2 indicates that, although a great deal of progress has been made, additional developmental efforts are required to translate promising laboratory results to prototype units from which realistic engineering and cost data can be generated. In general, the performance (power output) of the molten carbonate fuel cell is adequate to meet system requirements. As a result, the development should center on improving the endurance and providing manufacturable cell components for the engineering evaluation of prototype multicell fuel cell stacks. As stated earlier, the molten carbonate materials costs are reasonably low. However, the manufacturing costs of the electrolyte tile and the cell separator plate are high for present

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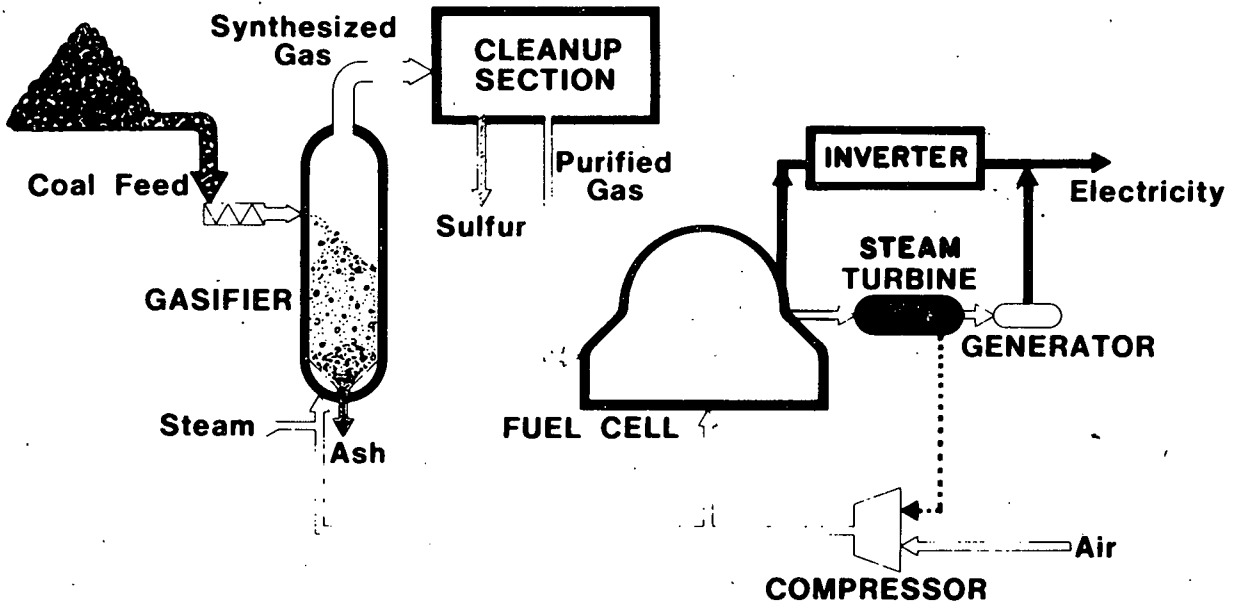
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Figure 1.   SCHEMATIC OF COAL-FUELED MOLTEN CARBONATE FUEL CELL SYSTEM

Table 2.   TECHNOLOGY CATEGORIES AND GOALS

Performance	650 mV (End of Life)
	160 mA/cm^2
	650°C
	10 atm
	75% Fuel Utilization
	50% Oxid. Utilization
Cost	$100/Stack kW (78$)
Life	40,000 hours (< 4mV/1000 hr)
	20 plus thermal cycles
Scale-up	700 Cell Stack
	2 ft by 2 ft or larger

Table 3.   ENDURANCE TESTING

Configuration	Hours	Terminations	Decay, mV/1000 hrs
Boiler Plate	15,000	Wet Seal Failure	~3*
Boiler Plate	10,000	Voluntary	9
Boiler Plate	10,000	Voluntary	8
Sheet Metal	3,000	Gas Crossover	<1
Boiler Plate	3,700	Voluntary	12

* Periodic additions of carbonate.

Table 4.   TECHNOLOGY STATUS SUMMARY 1959 TO 1980, LIFE LIMITATIONS

Item	Fix	10,000 to 15,000 hr Demonstration	40,000 hr Potential
Anode Sintering	Cr Stab.	Yes	Good
Carbonate Loss	Component Mod. Pressure	No	TBD
Wet Seal Corrosion	Aluminization	Yes	Excellent
Separator Plate Corrosion	Nickel or Nickel/SS	Yes	Excellent
Performance Decay	Carb Mgt. Stable Comp.	10 mV/1000	2.5 mV/1000 Desired
LiAlO$_2$ Stability	Doping & Pretreat	Yes	Good
Electrolyte Tile Cracking	Crack Arrestors Microstructural Improvements Bubble Barriers	No	TBD
Cathode Strength	Reinforcement Tape Casting Modified Thickness	No	TBD

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cell configurations. In addition, the electrolyte tile, probably the most critical cell component, needs further material and configuration development to achieve the endurance, cost, and system operational goals.

EXPERIMENTAL HARDWARE

The initial experimental screening of materials and concepts has been done primarily in circular cells of 3 cm^2 area. These are termed "laboratory cells" and are extremely reproducible and provide the unambiguous data needed to establish the fundamental relationships. After components have been qualified in laboratory cells, they are tested in larger cells, 94 cm^2 area, to determine performance and endurance, effect of process variables such as gas composition, temperature, and pressure, and stability of metallic cell components. These are termed "boiler plate cells" and can test critical components in a more realistic manner. Our baseline performance, which closely approaches the goals noted in Table 2, has been established in this configuration. Presently, we are in the process of developing the data base and experience which will allow the baseline performance to be obtained in cost-effective cell configurations. This configuration, termed "sheet metal," uses components that are more realistic in terms of cost and mass producibility for gas distribution, sealing, and current collection. Two sizes of "sheet metal" cells have been designed. One is the same as the boiler plate cell, 94 cm^2, and another has been scaled to 929 cm^2 (1 ft^2) preparatory to construction of cell stacks. No experimental testing of these 929 cm^2 sheet metal cells has yet been performed.

ENDURANCE

The laboratory-scale cells have surpassed 40,000 hours of life, thus establishing that critical components can be designed to perform adequately. Three boiler plate cells, 94 cm^2, have attained in excess of 10,000 hours. Performance of two cells is shown in Figure 2. The average degradation rate was 10 mV/1000 hr. These rates are roughly double the goal established for the system. A large part of this degradation is believed to result from a gradual electrolyte loss through vaporization. The approaches being taken to reduce this loss will be described in a later section dealing with the electrolyte tile. Most of the endurance testing has been performed at 1 atmosphere pressure; however, boiler plate cells operated at 5 and 10 atmospheres have exceeded 1000 hours of operation. Reproducibility of baseline (i.e., boiler plate) performance in sheet metal hardware has been mostly successful as demonstrated by that shown in Figure 3.

Operation at elevated pressure has a number of positive attributes — reduced electrolyte loss by evaporation, reduction in system volumes and thus reduction in cost of materials, and enhanced performance. This performance increase, typically in excess of 80 mV, exceeds that of 45 mV predicted by thermodynamics. Most of this additional increase is attributed to reduced polarization and enhanced reactant solubility. However, there are also drawbacks; one is the necessity for accurate pressure control to prevent an excessive differential across the tile; another is the loss of reactants by the formation of inert methane. That reaction ($2CO + 2H_2 \rightarrow CO_2 + CH_4$) is strongly pressure-dependent. Fortunately, the kinetics are not too rapid and equilibrium is seldom attained. Of greater concern is the possible deposition of carbon leading to blocking of the fuel distribution which leads to blocking of operation of the cells. That reaction ($2CO \rightarrow C + CO_2$) is also favored by a pressure increase. Prevention requires close monitoring and control of the fuel stream composition.
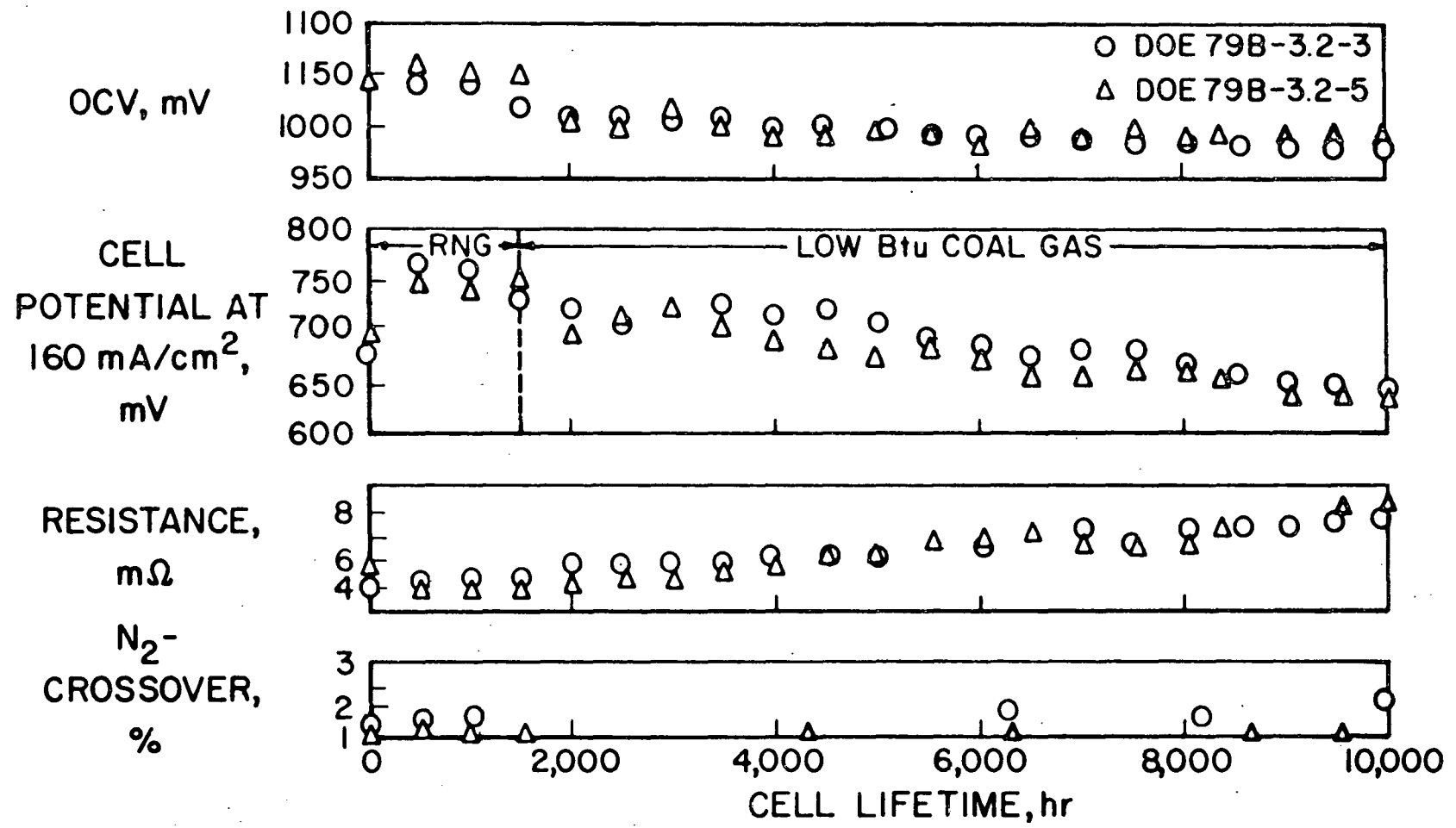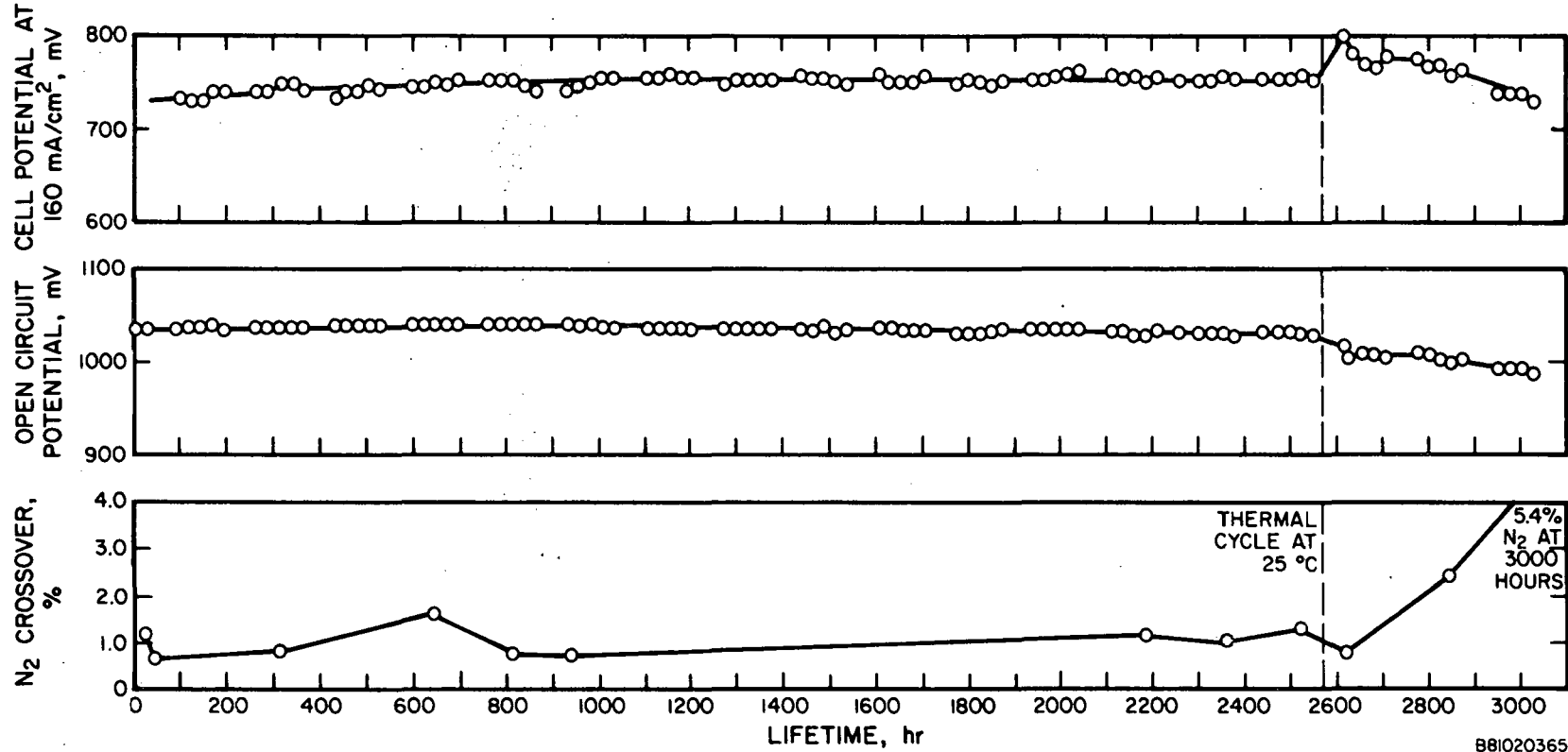
Figure 2. 10,000 HOUR ENDURANCE TESTING

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Figure 3. PERFORMANCE OF SHEET METAL CELL IGT-SM-1 AT 160 mA/cm² AND 650°C

FUEL COMPOSITION

The composition of the fuel stream entering the fuel cell depends upon the primary hydrocarbon fuel and the process selected for production of the hydrogen-rich stream. Steam reforming of methane yields a hydrogen-rich stream while an air-blown coal gasifier yields an inherently lower hydrogen stream further diluted by nitrogen. Fortunately, molten carbonate systems are not poisoned by carbon monoxide as are phosphoric acid cells. In fact, via the water gas shift production of hydrogen, carbon monoxide is consumed as fuel. However, the materials currently used in construction are extremely sensitive to the presence of sulfur-containing contaminants of the fuel, primarily H_2S and COS. Present emphasis is on reducing these contaminants to a tolerable level via a cleanup system, rather than using materials of construction that are tolerant of the untreated levels. Based on experimental results generated in an EPRI-funded program, it is believed the increase in materials cost would exceed that of gas cleaning. However, there is still a need to establish the long-term impurity level limits and the impact of short-term sulfur increases resulting from process upsets. Sulfur-containing contaminants primarily affect the anode performance, but if levels are not high and do not last long, the degradation observed is reversible once the level is reduced. This recovery is shown in Figure 5. Sulfur species not only cause harm when in the anode stream; if they are in the cathode stream, as SO_2, for instance, they react with the electrolyte, are transported through the electrolyte to the anode, where they are reduced, and behave as if originally present in that location. (See Figure 6.) Operation at an elevated temperature, say 700°C instead of 650°C, increases tolerance to H_2S and COS. This improvement in performance is shown in Figure 7. For COS, this improvement in anode tolerance was less than for H_2S at a comparable concentration. This could be used as a short-term control response to an upset, but the long-term disadvantages of increased corrosion, vapor loss, electrode sintering, and other effects are felt to outweigh continual operation above 650°C.

ELECTRODES

Based on experimental results, the endurance and performance of the chromium-stabilized nickel anode and the lithiated nickel oxide cathode are satisfactory for the present 40,000-hour goal. However, it is desirable to reduce the amount of nickel (one of the highest cost-per-pound materials used in the system) used for the anode and to improve the strength and structural integrity of the nickel oxide cathode. Efforts to reduce the amount of nickel are proceeding in two parallel paths — using less expensive alternative metals and reducing the amount of nickel by plating the nickel on inorganic structures. Initial efforts in both areas are showing promise. The cathode strength is being improved both by using alternative fabrication processes such as tape casting and by using metallic reinforcing.

ELECTROLYTE TILE

As stated earlier, the electrolyte tile is probably the most critical molten carbonate fuel cell component. It is a composite structure wherein a mixed alkali carbonate is contained by capillary forces within a finely divided inorganic matrix. This matrix material is presently $LiAlO_2$, though some effort is being expended by others on alternatives such as $SrTiO_3$. The chemical stability of $LiAlO_2$ is not in question; the physical stability is. Such a high surface material, in the range of 15-30 m^2/g, has the inherent tendency to sinter and reduce surface area. This increase in particle size, often accompanied by a change in phase from β to $\gamma+\alpha$, permits the electrolyte to have a greater and undesirable mobility. Methods of preparation yielding higher surface areas can result in an effec-
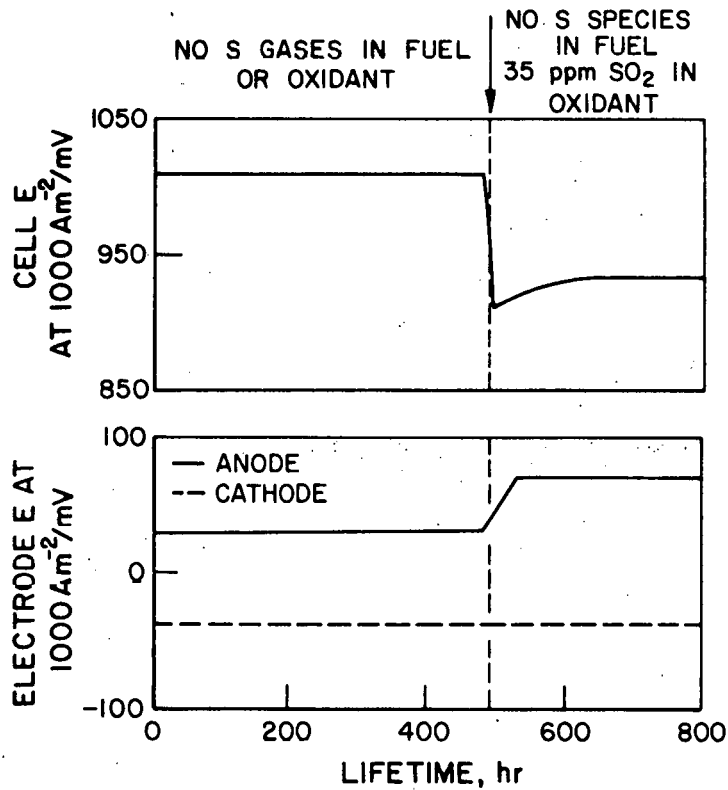
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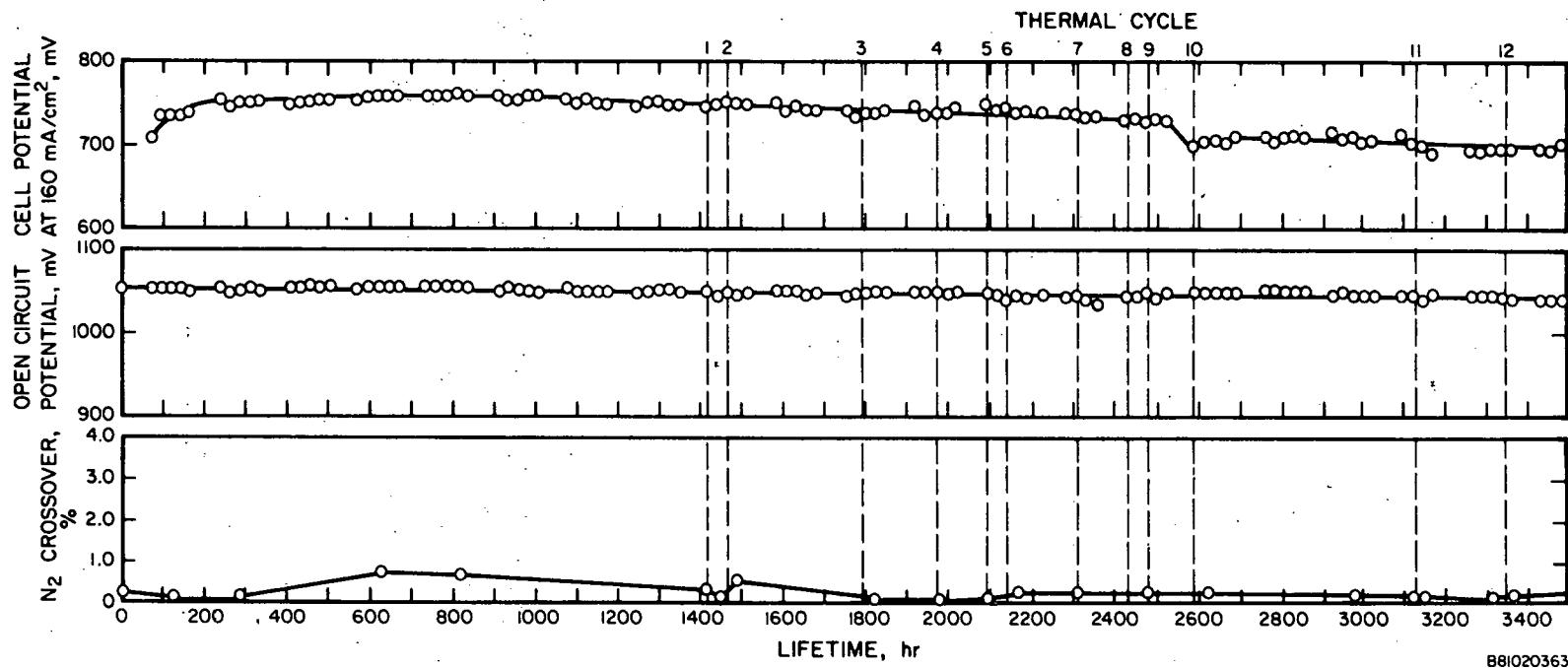
Figure 4. THERMAL CYCLING OF CELL IGT-BS-2 WITH TILE FROM SPRAY-DRIED POWDER (AD60-4A)
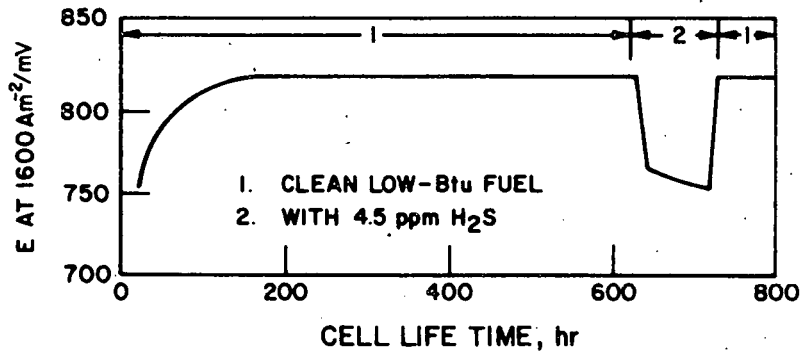
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Figure 5. RECOVERY OF CELL VOLTAGE ON REMOVAL OF H_2S FROM FUEL

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Figure 6. EFFECT OF SO_2 IN OXIDANT ON ANODE AND CATHODE POLARIZATION
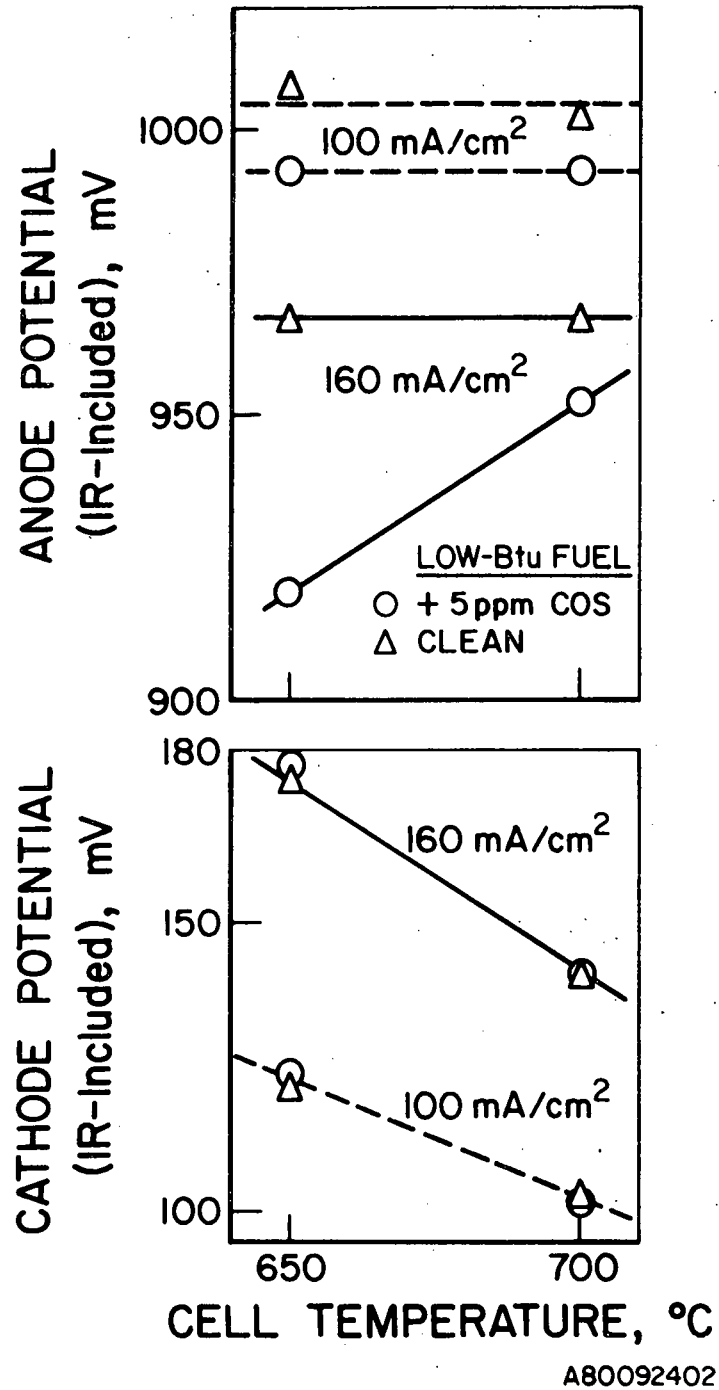
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Figure 7. EFFECT OF TEMPERATURE ON ANODE TOLERANCE OF CELL EPRI-24

tive immobilization for longer periods of time. If the log-log relationship between surface area and time, shown in Figure 8, is followed, then a minor increase in the initial area may yield a satisfactory life above some final value of surface area. Attempts to find dopants to reduce the sintering rate and/or affect the phase composition shift have not been completely successful.

The other major life variable of the electrolyte tile is the loss of the electrolyte, both through reaction with other components and by evaporation. This eventually leads to gas crossover resulting in inefficiency, an increase in local cell temperature, and a waste heat load. The relative losses via reaction and evaporation have been determined (Figure 9). It is projected that by preloading the electrodes with electrolyte before cell assembly, operating at pressure, and using a sodium-lithium carbonate mixture, sufficient electrolyte will remain for a 40,000-hour life. The sodium-lithium carbonate has a measured vapor pressure at 650°C that is approximately one-fifth that of the potassium-lithium carbonate in current use.

Alternative electrolyte compositions are being examined for performance improvements over the 62% Li_2CO_3/38% K_2CO_3 normally used. Highest performance has been obtained for high Li/K compositions and a high-lithium ternary mixture. However, the 52% Li_2CO_3/48% Na_2CO_3 mixture with the lower vapor pressure also has a slight reduction in performance. Since lithium is lost preferentially, all compositions will eventually drift toward sodium rich, if sodium is present, since it has the lowest vapor pressure. A more complete mapping of performance and component loss is required to establish the performance path the cell will take with time.

THERMAL CYCLING

The ability to sustain thermal cycles wherein the constrained electrolyte tile freezes and contracts without degradation is a basic requirement of a potential system. Fortunately, those synthesis efforts which have yielded higher surface area $LiAlO_2$ via a more reproducible and less expensive process have also resulted in a higher strength tile. This has enabled one cell to be cycled through the melting point 12 times without significant performance losses (Figure 4). The performance reduction at the unscheduled cycle 10 (about 2600 hours) resulted from a known change in operating conditions, rather than a tile failure. Further testing of broader temperature excursions and greater frequency is in process.

Comprehensive analytical studies have been completed to identify the source and magnitude of the thermally generated stresses causing tile cracking. Both the cell design and the materials used and the means of tile fabrication have a major influence on tile integrity. Neither approach by itself is sufficient to result in a functional tile which will prevent gas crossover. Therefore, in addition to using cell designs that minimize thermally generated stresses, we are improving the tile microstructure, using reinforcement materials, bubble barriers, and crack arrestors.

The technique of acoustic emission has been adopted to assist in evaluating many conceptual solutions in out-of-cell testing. A large increase in the magnitude and frequency of acoustic events at temperatures below the melting point, about 400°C, is clearly demonstrated by this means. Though there is some question in the interpretation of these events, this technique is being used to evaluate the effect of the inclusion of particles of various materials as crack arresters. The size and number of the particles and their chemical-physical bonding to the electrolyte are all variables needing quantification. Some materials have produced a clear decrease in both frequency and magnitude of acoustic events. It is
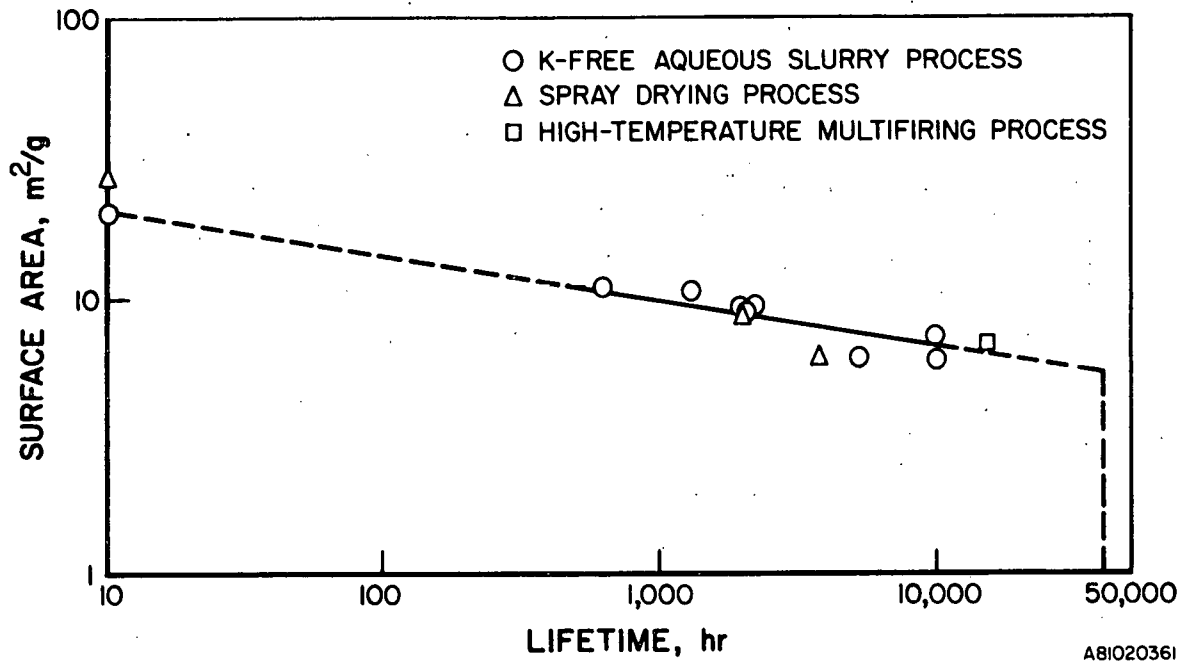
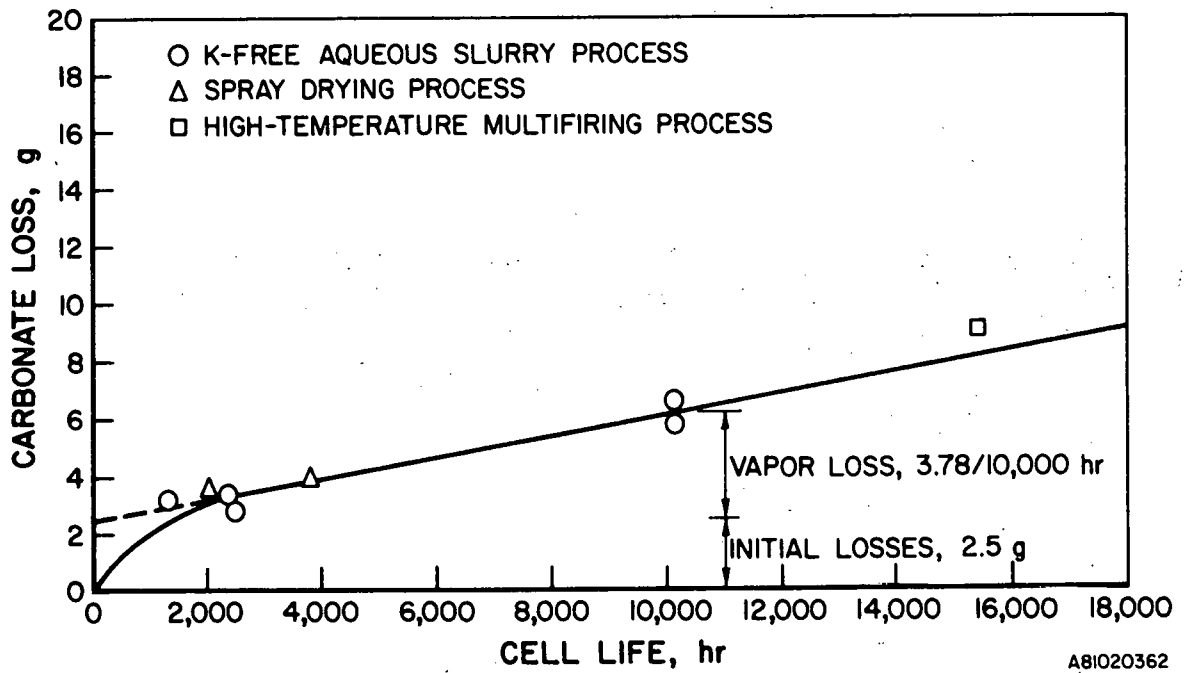Figure 8. LiAlO$_2$ SURFACE AREA LOSS IN 94 cm^2 CELLS

Figure 9. CARBONATE LOSS CURVE FROM STANDARD 94 cm^2 BOILER PLATE FUEL CELLS

hoped that relating all these will also improve the physical explanation of the events. This screening will be followed by in-cell evaluation of the better candidates.

CELL SEPARATOR

In a bipolar cell stack, each cell is separated from the next by a separator which serves as an electrical connection, a gas separator, and a gas distribution plate. The environment within which the cell separator must survive is extremely adverse. The ability to withstand the presence of reductants on one side and oxidants on the other, under a potential and exposure to an electrolyte, and yet maintain conductivity and be inexpensive and easily manufactured or formed — this is a severe set of requirements. For the short term, say 2000 hours, 316 stainless steel seems to adequately meet the above requirements. This material, in 10 mil sheets, is being formed into the corrugated structure that provides for gas distribution without an excessive pressure drop. The electrode strength dictates the spacing of the ribs and this, in conjunction with the material properties and thickness, controls the height. These rib dimensions are 120 mil pitch and 58 mil height. Figure 10 is a cross-section showing the tolerances maintained during pressing. For lifetimes exceeding 20,000 hours a stable material is required on the anode side, and the logical though expensive choice is a composite with nickel. This may not require a large and costly amount and alternatives may also be found, such as those being sought for the anode. It is likely that the process for forming and subsequent treatment of such a composite will have a pronounced effect on its performance and stability in the cell environment.

A further critical environment is the wet-seal area where the separator contacts the electrolyte tile. In stack designs, exposure of the separator in this area to the reactants will create an electrochemical cell that results in rapid corrosion unless insulated. Alumina or aluminum (later oxidized) or NiAluminide are satisfactory; however, methods of fabrication strongly influence adherence and density and thus stability.

SCALE-UP

Prior to the eventual manufacture of large-scale cells and stacks, some emphasis on small stacks of 1 ft^2 active area can provide an insight into the fundamental problems inherent in cell stacking. The selection of external gas manifolding provides for a design alternative to the internal manifolds being designed by GE. The cell package and stack design to be constructed in early FY82 are shown in Figures 11 and 12. That 20-cell stack will produce in excess of 2 kW and will be thermally self-sustaining.

General Electric will be producing cells larger than 4 ft^2 to more closely approximate, if not represent, preproduction prototypes. They have successfully pressed and handled electrolyte tiles 50 by 50 inches. Based on uniformity and reproducibility, a final cell size somewhere between 4 and 16 ft^2 will be selected for an eventual 70 cell stack which provides one-tenth of the output of an ultimate production stack.

CONCLUSIONS

The progress of the DOE and EPRI funded programs has been substantial, and a number of very productive concepts and major accomplishments have been realized. Though it would be presumptous to state that all the problems are recognized and being addressed, those that are being addressed seem to have identifiable and promising technical solutions. Admittedly, the economics of these solutions are less certain.
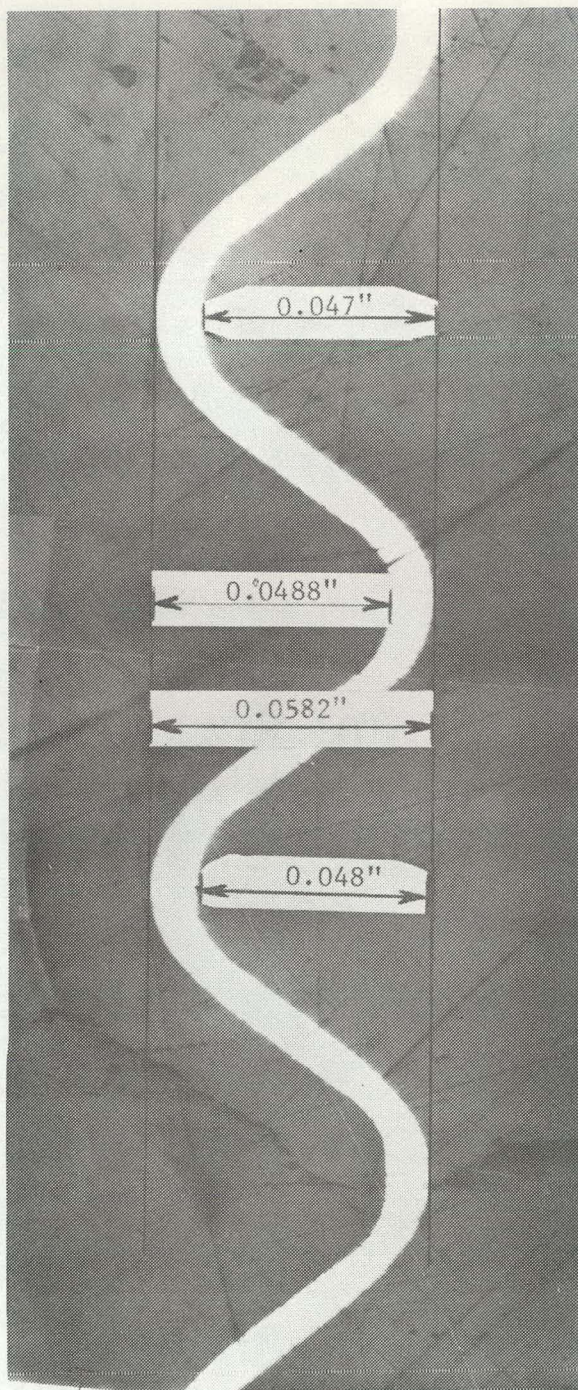
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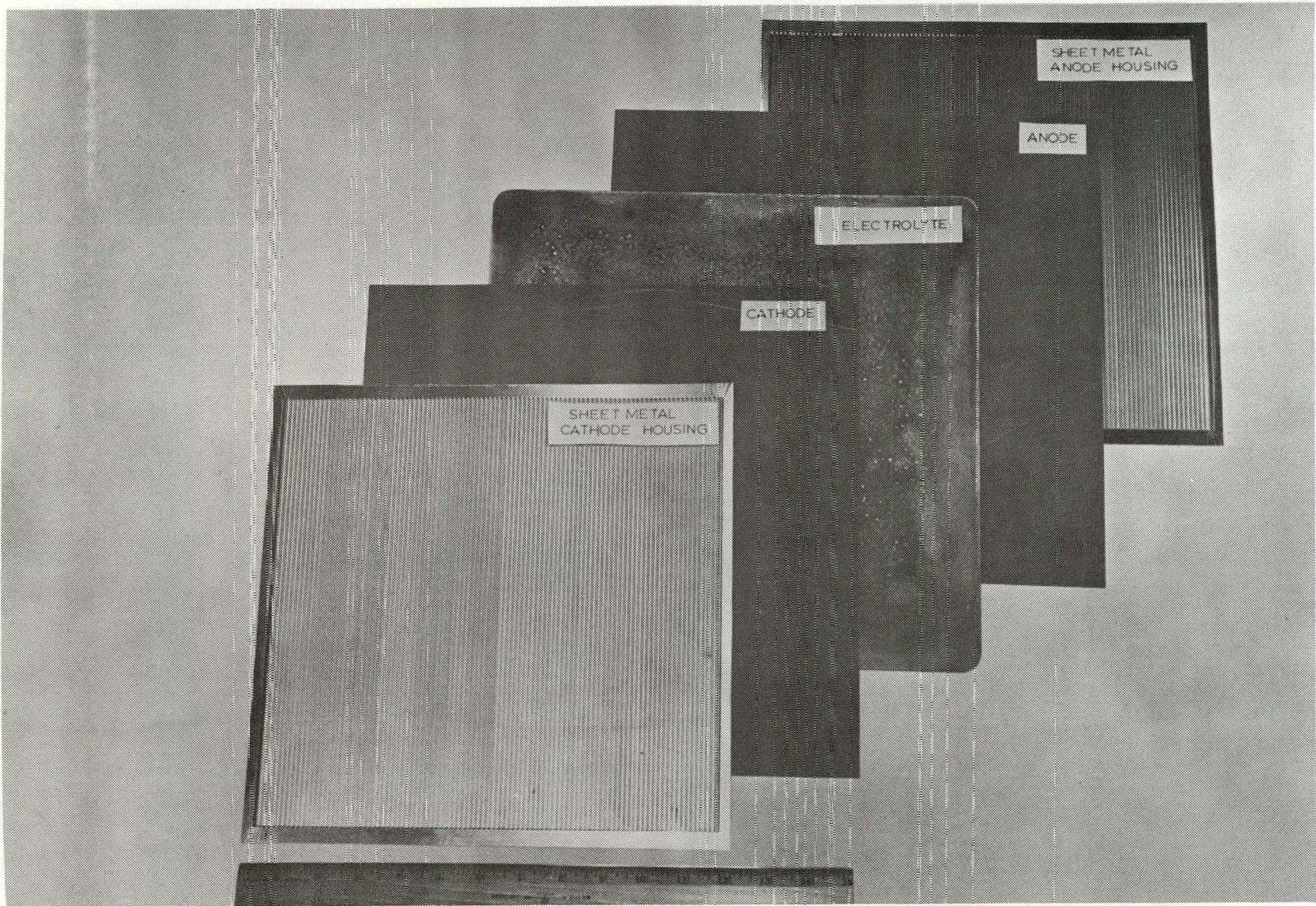Figure 10.   CROSS SECTION OF BIPOLAR PLATE FOR MCFC STACK
(Material: Type 316 S.S.)

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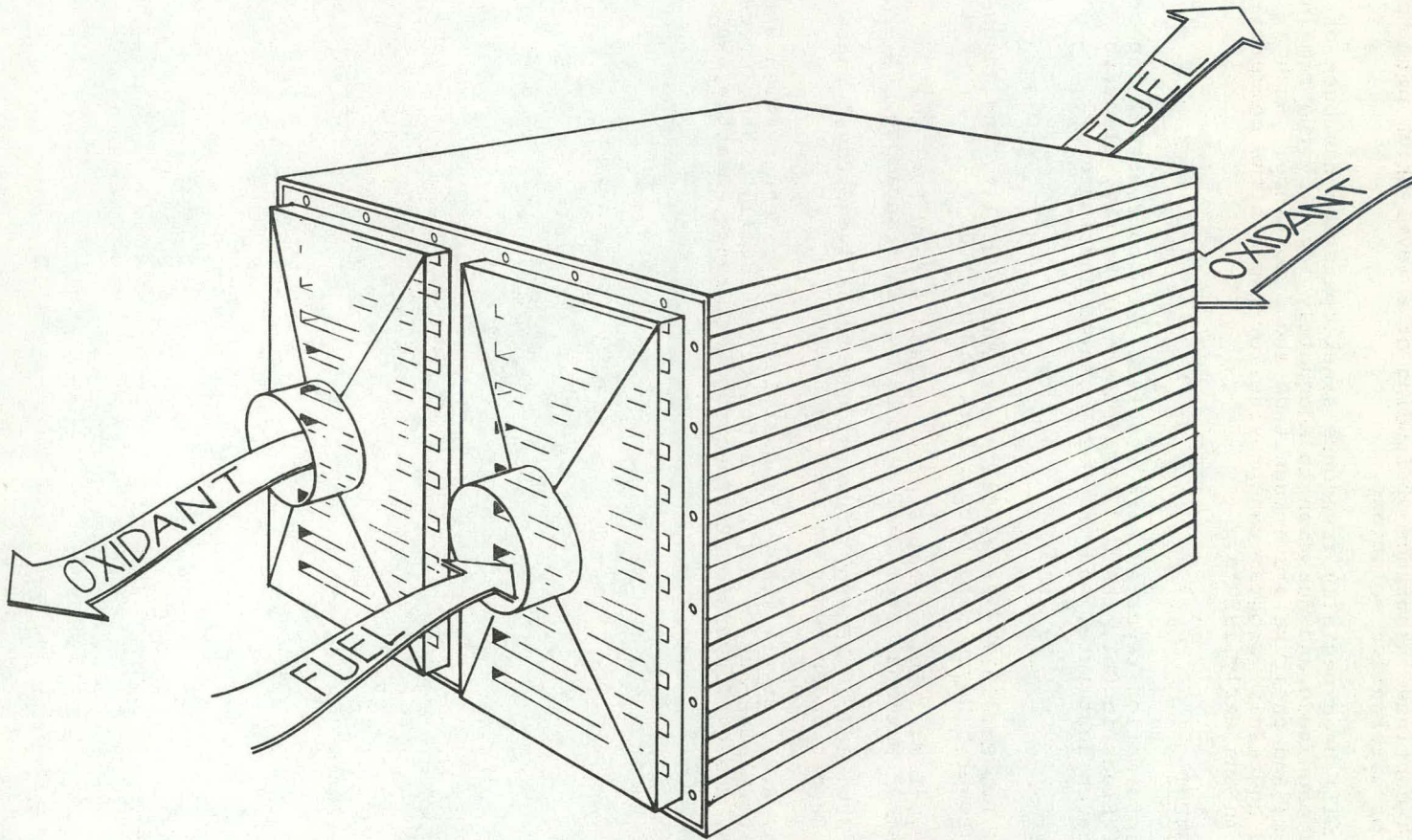Figure 11. DESIGN FOR 2-kW CELL STACK USING 1-ft^2 SHEET METAL

Figure 12.   X-CONFIGURATION EXTERNAL GAS MANIFOLDING

There are a number of creative and technically competent firms involved in the establishment of an efficient and economic means of power generation via molten carbonate fuel cells. What is critically needed is a continued assurance of funding at a level which permits pursuance of alternative solutions.

This will be especially true once stack operation has been of sufficient magnitude and duration to adequately identify the remaining problems and their relative magnitude and importance. Such a stable and aggressive program can provide for expeditious commercialization in the early 1990's.

ACKNOWLEDGMENT

REFERENCES

1. Noyes, R., Ed. 1977. "Fuel Cells for Public Utility and Industrial Power," Noyes Data Corp., Park Ridge, N.J.

2. Handley, L.M. 1978. "Status of 40-kW and 4.8-MW Fuel Cell Programs," National Fuel Cell Symposium, San Francisoco, CA.

3. King, J.M. 1975. "Energy Conversion Alternative Study," Phase II Final Report under contract NAS3-19586.

4. Bowman, R.M., et al. 1980. "Industrial Energy Conservation with the Natural Gas-Fueled Molten Carbonate Fuel Cell," 15th Intersociety Energy Conversion Engineering Conference, Seattle, WA.

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