DEVELOPMENTAL STATUS AND SYSTEM STUDIES OF THE MONOLITHIC SOLID OXIDE FUEL CELL

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Kevin M. Myles
Electrochemical Technology Program
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439, U.S.A.

ABSTRACT

The monolithic solid oxide fuel cell (MSOFC) was invented at the Argonne National Laboratory in 1983 and is currently being developed by a team consisting of Argonne National Laboratory and Allied-Signal Aerospace/AiResearch. The MSOFC is an oxide ceramic structure in which appropriate electronic and ionic conductors are fabricated in a "honeycomb" shape similar to a block of corrugated paperboard. The electrolyte, which conducts oxygen ions from the air side to the fuel side, is yttria-stabilized zirconia (YSZ). All the other materials, that is, the nickel-YSZ anode, the strontium-doped lanthanum manganite cathode, and the doped lanthanum chromite interconnect (bipolar plate), are electronic conductors. These electronic and ionic conductors are arranged to provide short conduction paths to minimize resistive losses. The power density achievable with the MSOFC is expected to be about 8 kW/kg or 4 kW/l at fuel efficiencies over 50 percent, because of small cell size and low resistive losses in the materials. These performances have been approached in laboratory test fuel cell stacks of nominal 125-W capacities.

1. STACK FABRICATION

The MSOFC was originally tape cast, but currently it is hot roll calendered. The hot roll calendering process, shown in Fig. 1, consists of mixing ceramic powder with organic binder and plasticizer and rolling the warm mixture into a thin tape. The "green" tapes are cut to the desired dimensions, and the electrode tapes are corrugated to form the gas flow channels. The corrugations are formed by folding the tape onto a warm mold. The corrugated electrode tapes and the flat electrolyte and interconnect tapes are stacked up in sequence to form the MSOFC structure. The layers are bonded together in the green state and the entire structure is then heated, according to a precise firing schedule, to the sintering temperature of about 1300-1400°C in order to form the "monolithic" ceramic structure. The shrinkages that occur during binder burnout and during sintering are precisely matched among the four component materials.

The interconnect can be fabricated separately from the other layers to allow higher sintering temperatures, eliminate shrinkage mismatches, and stop liquid-phase wicking, which hinders interconnect densification. While the interconnect, cathode, and electrolyte have high processing yields, the anode sheets have roughly a 60 percent processing yield. This lower yield could be caused by variations in the thermal expansion within the anode layer that result from a nonuniform distribution of nickel.

Because of the inherent brittleness of ceramics, microstructural cracks are unavoidable in the components of the MSOFC. The presence of large failure-causing microstructural cracks is a potential problem because these cracks could propagate through the electrolyte and interconnect layers, as a result of fuel cell operation and thermal cycling, and allow leakage between the fuel and

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air passages. The structural integrity of the MSOFC has been maintained by increasing the resistance to crack propagation and by minimizing the subcritical growth of inherent cracks by developing microstructures with improved fracture toughness. Fracture toughness has been improved by the addition of second-phase particles that act as crack arresting sites. The second-phase particles also induce microcracking in the matrix phase by providing a critical strain mismatch between the matrix and the second phase that with appropriate size and population density can absorb strain energy. In the past, both crack pinning and microcracking techniques have been successfully used to fabricate tape cast ZrO_2-based composite electrolytes with much improved fracture toughness. The feasibility of applying these techniques to calendered materials is being evaluated. Analytical analysis of the stress patterns in the MSOFC is in progress to predict the stresses incurred during fabrication and operation of the stack. Comparative analyses using an elastic model and the ANSYS stress model have yielded essentially identical results.

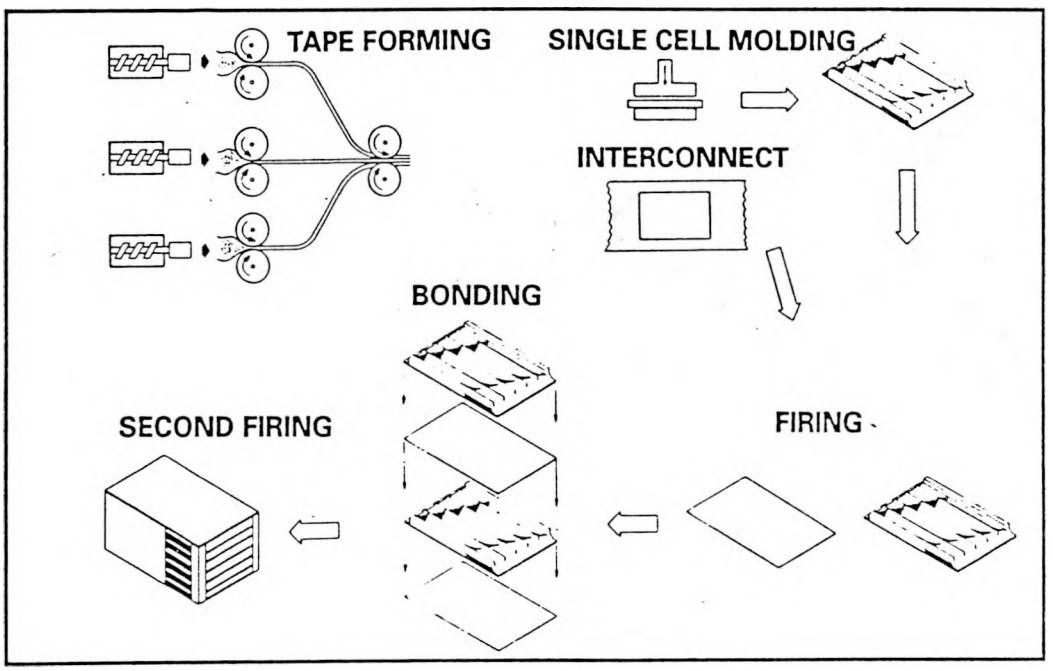
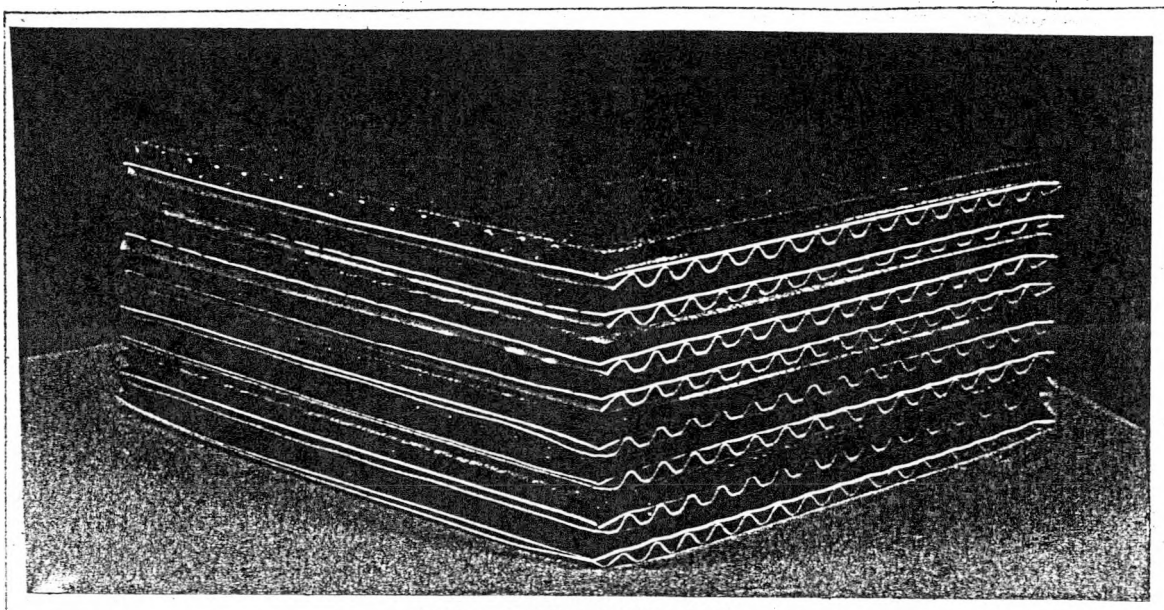


Figure 1. Schematic of Hot Roll Calendering.

To date, many three-cell stacks and several eight- to ten-cell stacks have been fabricated with the tape cast components. Two-cell stacks and 50-W and 100-W (projected power) stacks have been fabricated with the hot roll calendering process. A photograph of the 50-W stack (cross-flow design) is shown in Fig. 2. A design of a 100-W stack that includes the fuel and oxidant manifolds is shown in Fig. 3.



1.5 in x 1.5 in x 0.75 in high

Figure 2. Cross-flow MSOFC Stack as Fabricated by Allied-Signal Aerospace/AiResearch.

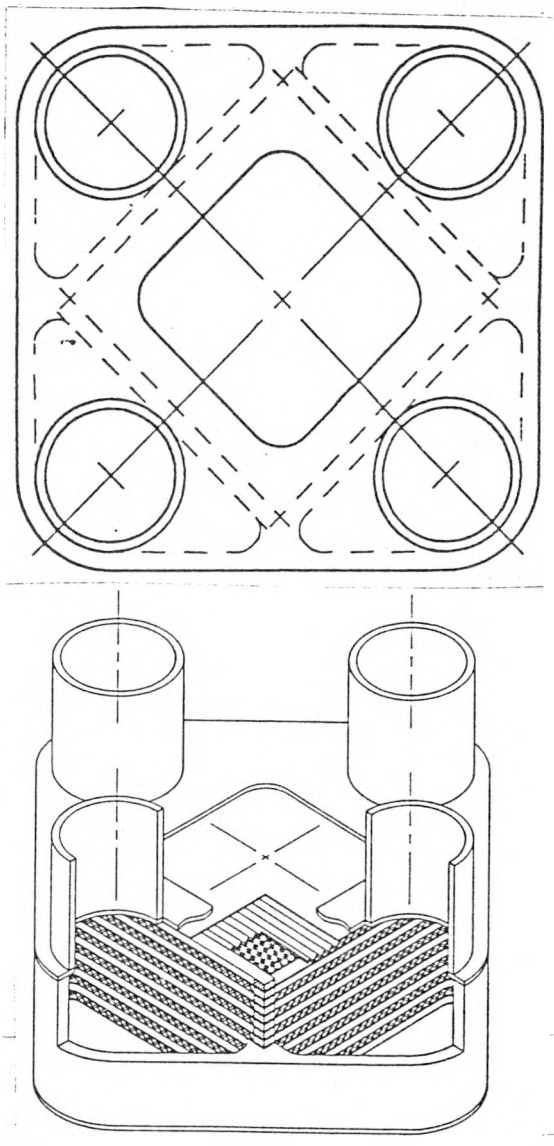


Figure 3. Cutaway View of 100-W MSOFC Stack with Fuel and Oxidant Manifolds.

2. PERFORMANCE

The performance of the MSOFC has improved significantly during the course of development. Tests have been performed at 1000° C with both hydrogen and simulated coal gas as the fuel and with both pure oxygen and air as the oxidant. The results, as shown in Fig. 4, indicate that, for the fuel compositions evaluated, oxygen roughly doubles the achievable current density and hence the power. The limitation of the MSOFC, based on the resistance of the materials alone, without interfacial resistances, is about 0.05 Ω cm^2. With further development, the area-specific resistance (ASR) is expected to be reduced to 0.1 Ω cm^2, which will result in power levels greater than 2.5 W/cm^2. Reducing the ASR even more will require that the electrochemically-active areas within the electrodes be increased. At present, the factors that control the kinetics of the electrochemical process are only poorly understood. In addition to these fuels, various hydrocarbon fuels have been rapidly reformed within the nickel-YSZ fuel channels.

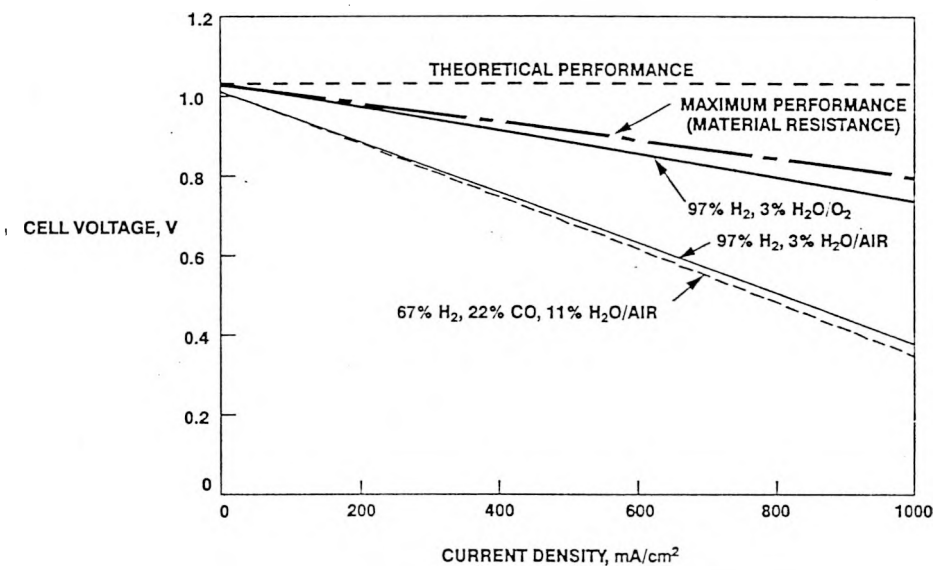


Figure 4. MSOFC Cell Performance.

The difference between single-cell and multi-cell stack performance is primarily due to interactions among the materials during the sintering process. A liquid-phase sintering aid is used to assist densification of the interconnect material. This sintering aid migrates throughout the MSOFC structure and affects the other materials, particularly the cathode. The cathode becomes dense and tends to migrate away from the electrolyte/cathode interface, leaving voids in that critical area. This effect on the cathode reduces the performance of the multi-cell stacks. Alternative materials to the conventional strontium-doped lanthanum chromite are being developed to enhance the sinterability and conductivity of the interconnect material. Both $La_{0.8}Ca_{0.2}Cr_{0.9}Co_{0.1}O_3$ and $Y_{0.8}Ca_{0.2}Cr_{0.9}Co_{0.1}O_3$ have proven to dramatically increase the air sinterability of the interconnect at 1400° C especially when formed with ultra fine powers.

3. MATERIALS

Because state-of-the-art SOFCs operate at 1000° C, the design of the fuel cell has to incorporate materials that are stable, both chemically and thermally, and mechanically strong under harsh conditions. Indeed, the number of materials that can be used is quite limited. Further, the air and fuel streams have to be preheated to nearly 1000° C to avoid exasperating the thermal stresses in

the fuel cell stack. Operating the SOFC at lower temperatures, such as 600-800° C, would lessen these issues and allow much greater flexibility in engineering the stack because metals might be able to be used as interconnect and gasket materials. Interdiffusion between cathode and electrolyte, which occurs at 1000° C, would be minimal while internal fuel reforming would still occur.

The conductivity of the electrolyte determines the operating temperature of the fuel cell. Unfortunately, the yttrium-doped zirconium oxide (YSZ) electrolyte has only a conductivity of 4 x $10^{-2}/\Omega$ cm at 800° C, which is too low for a high-performance fuel cell. Accordingly, an effort to find new, more highly-conductive electrolytes has been initiated.

The mechanism of ion conduction in a solid depends on the crystallographic structure and morphology of the solid. Amorphous solids like "Nafion" conduct by a different mechanism than crystalline solids like YSZ. This present study evaluated crystalline minerals that were doped with lower valent elements to create oxygen vacancies to which oxide ions can migrate by sequentially jumping from site to adjacent site (see Fig. 5). Additionally, minerals in which the mechanism for ion transport is the migration of mobile counter ions through a fixed framework of charged sites, such as β"-Al_2O_3, (see Fig. 6), were also evaluated.

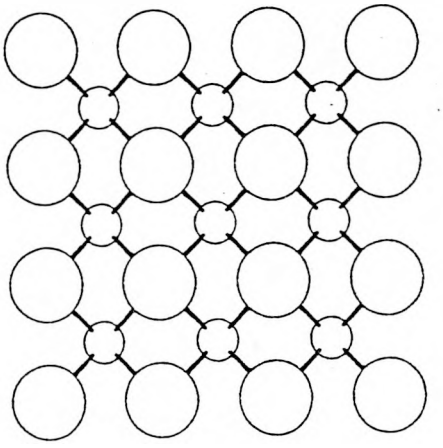


Figure 5. Crystal structure of the cubic form of ZrO_2.

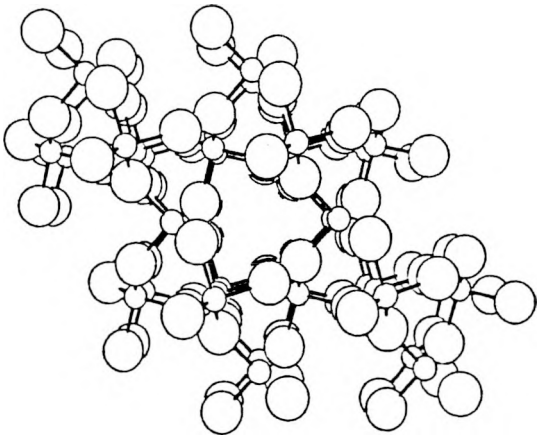


Figure 6. Crystal structure of the hexagonal form of $AlPO_4$.

The mineral types screened along with the proposed ionic transport mechanism is given in Table 1. Whereas the conductivity of a large number of compositions of these minerals with various

dopants have been studied, perhaps the highest conductivities at 800° C were found in samples of 1:1 mixture of the P-doped perovskite $BiAlO_3$ and $Bi_2Al_4O_9$ with a conductivity of 7.5 x $10^{-2}/\Omega$ cm, as measured by AC impedance spectroscopy, and an ionic transference number of 0.6. This conductivity approaches our initial goal of equaling the conductivity of YSZ at 1000° C (10 x $10^{-2}/\Omega$ cm). The thermodynamic stability of the compounds in the environments of the fuel cell electrodes is also being evaluated.

Table 1. Minerals Screened

Mineral	Example	Mechanism of Ionic Transport
Perovskites	$SrZrO_3$	Oxide ion, proton, hydroxide, or vacancy migration
Orthophosphates	$AlPO_4$, $LaPO_4$	Ionic migration through central channel in crystal structure.
Apatites	$Sr_{10}(OH)_2(PO_4)_6$	Ionic migration through central channel in crystal structure.
Garnets	$Y_3Al_5O_{12}$	Migration of vacancies through open space in structure.
Scheelites	$Nd_2(WO_4)_3$	Ionic migration along planes of WO_4

4. SYSTEM FOR TERRESTRIAL TRANSPORTATION

A conceptual methanol-fuel-based cross-flow MSOFC system designed for terrestrial transportation applications is shown in Fig. 7. The system has a 60-kW sustained power with a maximum power output of 75 kW and internally reforms the methanol/water fuel. Sixteen stack modules, described in Table 2, are arranged into a single, insulated unit. While this modular concept complicates the manifolding and electrical connections somewhat, it allows for a system with smaller fuel cell stacks that can be fabricated much more easily and reliably.

The incoming fuel is evaporated using residual heat from the spent fuel system. The incoming fuel flows through an eductor where a fraction of the spent fuel is caused to recirculate to provide heating and sufficient water for the reform reaction. The remaining spent fuel flows to the spent fuel burner where it is combined with the air exhaust stream, and the heat from burning the spent fuel is used to preheat the incoming air. The preheated air is further heated by recirculating most of the hot air exhausted from the fuel cell. This air recirculation is possible because very little of the oxygen is used in the electrochemical reaction. The primary function of the air flow is to remove waste heat from the fuel-cell core. Recirculating about two-thirds of the air minimizes the size of the air preheater heat exchanger. In terms of size and weight of components, the fuel cell and air preheater are approximately the same, and the other components are considerably smaller. All the components shown in the flow diagram are enclosed in a high-temperature insulated box, and other components such as the fuel pump, air blower, and control systems are essentially at room temperature.

Since the volume-power density of this MSOFC system is approximately 1 kW/l, the 60-kW (electric) system occupies about 60 l volume (about 2 ft^3). When the fuel cell operates at full power, the temperature of the downstream region rises dramatically due to the generation of waste heat. Because vehicle driving profiles typically require rapid shifting from high power to low power and

vice versa, the MSOFC materials must be able to withstand rapid temperature oscillations. The thin sections and honeycomb structure of the MSOFC are particularly adapted to these rapid temperature changes. The coefficients of thermal expansion of the four materials used in the MSOFC are well matched; thus, changes in temperature do not cause significant stresses between the layers.

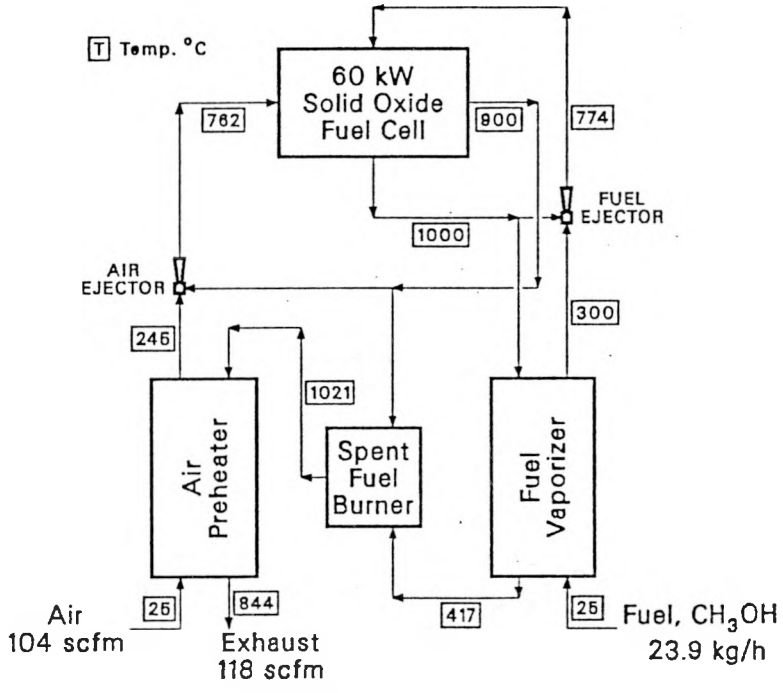


Figure 7. SOFC System for Transportation Application

Table 2. Monolithic SOFC Stack Module Design

Stack Power, kW	3.75
Current Density, A/cm^2	0.735
Gas Passage Height, mm	0.7
Area Specific Resistance, Ω-cm^2	
Materials	0.122
Interfacial	0.150
Air Flow (x Theoretical)	4.00
Fuel Utilization, %	85
Pressure Drop, psi	
Air	0.43
Fuel	0.31
Stack Dimensions, cm	
Length	13.2
Width	8.9
Height	13.3
Stack Power Density, kW/l	2.32

The thermal balance calculations for the MSOFC system are contained in Table 3. An efficiency of nearly 40 percent is obtainable at the 60-kW level. By virtue of the nonlinear reduction in the irreversible power losses in the fuel cell (I^2R) the system efficiency increases with decreasing power output.

Table 3. Thermal Balance of MSOFC System

	Power Level	
	60 kW	25 kW
CH_3OH Feed, kg/h	23.9	8.2
Energy Input (HHV), kW	150.8	51.6
Cell Energy Losses, kW		
$T\Delta S$	47.0	16.15
I^2R	20.0	2.35
Heat Duties, kW		
Fuel Vaporizer	15.3	5.2
Air Preheater	15.5	9.7
Spent Fuel Burner	22.6	7.7
Air Supply Blower Power, kW	1.17	0.42
Net Power, kW	60.0	25.0
Efficiency, %	39.9	48.6

The specific power of the entire assembly is 0.5 kW/kg. The system components have been designed to be integrated into a compact package and placed within a vacuum insulated casing to reduce heat losses so that the system can be kept in standby mode by consuming only approximately 0.5 kg of fuel per day.

5. ACKNOWLEDGMENTS

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