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MONOLITHIC SOLID OXIDE FUEL CELL DEVELOPMENT

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INTRODUCTION

The Monolithic Solid Oxide Fuel Cell (MSOFC) is being developed by a recently formed team consisting of Argonne National Laboratory, Allied-Signal Aerospace/AiResearch, and Combustion Engineering. The MSOFC (ref. 1) 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 that conducts oxygen ions from the air side to the fuel side is yttria-stabilized zirconia (YSZ). All the other materials are electronic conductors, including the nickel-YSZ anode, the strontium-doped lanthanum manganite cathode, and the doped lanthanum chromite interconnect (bipolar plate). 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 (ref. 2) at fuel efficiencies over 50%, because of small cell size and low resistive losses in the materials. The MSOFC operates in the range of 700 to 1000°C, at which temperatures rapid reform of hydrocarbon fuels is expected within the nickel-YSZ fuel channels.

Tape casting (ref. 3) and hot roll calendering (ref. 4) are used to fabricate the MSOFC structure. The tape casting process consists of spreading a ceramic slurry (slip) uniformly on a substrate, such as glass or polymer film, using a doctor blade. After the slip is dry, the ceramic layer is stripped off the substrate in the form of a flexible "tape." The hot roll calendering process 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. After cooling, the tape retains the corrugated shape. Corrugated electrode tapes and flat electrolyte and interconnect composite tapes are stacked up to form the MSOFC structure. The layers are bonded together in the green state by heating the polymer binder slightly above its glass transition temperature under a small weight. The bonded green structure is then heated according to a precise firing schedule to the sintering temperature to form the monolithic ceramic structure.

The performance of the MSOFC has improved significantly during the course of development. The limitation of this system, based on materials resistance alone without interfacial resistances, is 0.05 ohm-cm^2 area-specific resistance (ASR). The current typical performance of MSOFC single cells is characterized by ASRs of about 0.4 to 0.5 ohm-cm^2. With further development, the ASR is expected to be reduced below 0.1 ohm-cm^2, which will result in power levels greater than 2.5 W/cm^2.

SYSTEM PERFORMANCE

Because of the high temperature of operation of the MSOFC and the compact fuel cell design, systems that incorporate the MSOFC for power production are very simple. The high temperature combined with use of nickel in the fuel electrode allows internal reform of hydrocarbon fuels within the fuel channels, obviating the need for a separate fuel reformer. In addition, existing fuel logistics systems can be used with the MSOFC with essentially no modifications. Space-based systems that are required to regenerate the hydrogen fuel from the reaction product water are simplified by the fact that the MSOFC can use the same unit for power production and fuel regeneration. The high operating temperature of the MSOFC allows the waste heat to be rejected at a high temperature, thus minimizing the size of the heat rejection system. The MSOFC systems are flexible in terms of their ability to operate as an open cycle, closed cycle, or a combination of open and closed cycles.

Two types of systems are briefly described in the following paragraphs: (1) a power system for terrestrial vehicle propulsion using hydrocarbon fuel, and (2) an open-cycle, pulse-power system for use in space. Figure 1 is a schematic flow diagram of a 60 kWe vehicle propulsion power system designed to operate on a methanol/water solution. The 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 equivalent, and the other components are considerably smaller. All the components shown in this 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.

The volume power density of this system is approximately 1 kW/L, so the 60 kWe system shown in figure 1 occupies about 60 L volume (~2 ft^3). Operation of the MSOFC system for vehicle propulsion will require tolerance to rapid changes in thermal gradients. When a fuel cell operates at full power, the temperature of the downstream region rises due to generation of waste heat. Operation of the fuel cell at low power produces a shallow temperature gradient because the quantity of waste heat is low. Vehicle driving profiles typically require rapid shifting from high power to low power and vice versa. Because the temperature gradients will change as the power level changes, 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 (ref. 5); thus, changes in temperature do not cause significant stresses between the layers.

Coupling a nuclear reactor with a MSOFC appears attractive for space-based pulse power systems. The MSOFC combines hydrogen and oxygen to produce the power pulse, and the product water is stored on board. Following a test power pulse, the fuel cell is run in reverse to regenerate the hydrogen and oxygen. A relatively small nuclear reactor provides the power input for the reverse operation. Reject heat from the reactor may be used to maintain the fuel cell in a "hot standby" mode for rapid response to demands for power.

The hydrogen and oxygen are stored as gases in tanks at elevated temperatures and pressures, as shown in figure 2. Emerging from the storage tank, the oxygen stream passes through a blower and is preheated by mixing with an oxygen recycle stream before entering the fuel cell. Similarly, the hydrogen passes through a blower and preheater before entering the fuel cell. Within the fuel cell, DC power is produced as oxygen is consumed and hydrogen is converted to water vapor. The heat generated in the process is rejected as the oxygen recycle stream passes through the radiator. After a reduction in temperature, the gaseous products are stored. A sliding seal (or rolling diaphragm) is used to separate reactants and products which are stored within the same tank.

The system can be operated in the reverse mode to regenerate the power capability. The same monolithic fuel cell modules can be run backwards for the regeneration: a separate electrolysis unit is not required. The length of time required for regeneration is determined by the size of the external power source. The overall efficiency of the system is attractive. The projected performance of the system is to recover 72% of the heat of reaction in the discharge mode and store 92% of the input electrical energy as chemical energy in the electrolysis mode. The overall round-trip electrical efficiency is projected to be 66%.

The open-cycle concept is much simpler in system design and operation. A simple once-through system that has excess hydrogen available for cooling the fuel cell and for providing the chemical energy for the electrochemical process is shown in figure 3. The waste heat is carried out of the fuel cell core with the hydrogen stream, and the hydrogen and product water are dumped overboard. The oxygen stream is recycled with only a small bleed stream to eliminate any impurities that might accumulate. The system components include heat exchangers to heat the incoming oxygen using waste heat from the fuel cell exhaust streams, an eductor to recycle the hydrogen stream, and the fuel cell. Other components include the insulated box, current collectors, and appropriate control systems.

This very simple system has application only in very special cases where very high power densities are needed and an essentially "unlimited" source of hydrogen is available. Specialized space power systems are the only currently known applications for such a system, and this concept offers an interesting example of a compact, high power density system for space. The power densities that can be achieved with the MSOFC in this application are shown in figure 4. The fuel cell power density is shown on the left y-axis, while the system power density is shown on the right y-axis. The fuel cell power density is very high because the fuel utilization is very low. Essentially pure hydrogen exists through the whole length of the fuel channels, and the average Nernst potential is about 1 V. For these calculations, the area-specific resistance was assumed to be 0.05 ohm-cm^2, which is expected to be achieved with further development of the MSOFC. An important feature of the system is the relationship between the fuel cell power density and the system power density. As the fuel cell power density becomes larger, the contribution of the balance-of-system begins to dominate the system weight. The fuel cell weight becomes small relative to the balance-of-system when the fuel cell power density exceeds about 20 kW/kg. For this system design, the system power density approaches

~4.5 kW/kg as an upper limit, and this power density is determined by the sizes of the heat exchangers required to heat the incoming hydrogen and oxygen and the insulating box for the high-temperature components.

MSOFC FABRICATION

The principal challenge to fabrication of the MSOFC structure is to match the sintering shrinkages of the four MSOFC materials: (1) the electrolyte, yttria-stabilized zirconia, (2) the interconnect material, strontium-doped lanthanum chromite, (3) the anode material, nickel-zirconia cermet, and (4) the cathode material, strontium-doped lanthanum manganite. The MSOFC structure is assembled while the tape-cast components are in an unfired (green), flexible state. The polymer binder in the tapes bond the tapes together as they are placed in contact and heated above the "glass transition" temperature of the polymer. The assembled structure is then appropriately supported and heated slowly to burn out the polymer. The structure is further heated to temperatures of about 1300 to 1400°C to sinter the materials and create permanent bonds at the points of contact. It is important that the shrinkages that occur during binder burnout and during sintering be precisely matched among the four materials. This matching of shrinkages has been accomplished satisfactorily during development of the MSOFC, and the results of this shrinkage matching are reported elsewhere (ref. 5).

One of the important objectives in development of the MSOFC has been reduction of the number of defects in the ceramic structure. Defects such as cracks allow the fuel and oxidant gases to mix, thus reducing the efficiency and, if the cross-leakage is severe, reducing the open-circuit potential. Defects such as non-bonds between the layers increases the overall fuel cell resistance because of the reduced cross-section of the conduction path. As the sintering shrinkages and the coefficients of thermal expansion have become better matched, the performance of the fuel cells have improved. For example, the improvement in open-circuit voltage with reduced number of cracks in the fuel cell is shown in figure 5. The large number of cracks during the early development stages of the MSOFC caused sufficient cross-leakage of fuel and oxidant to reduce the difference in oxygen potential across the electrolyte. Since the Nernst potential is proportional to the log of the ratio of oxygen partial pressure in the oxidant to that in the fuel, the open-circuit voltage decreases with increased cross-leakage. The current status of MSOFC development is such that essentially crack-free structures can be built and tested.

MSOFC PERFORMANCE

The performance of the MSOFC has approached the theoretical limit as a result of recent development efforts. The first MSOFC single cells had an area-specific resistance (ASR) of about 8 ohm-cm^2, and since that time the performance has improved dramatically to the present state-of-the-art ASR of about 0.4 ohm-cm^2. The theoretical limit of performance, based on materials resistances and elimination of all electrode/electrolyte interfacial resistances, is about 0.093 ohm-cm^2 for an electrolyte thickness of 50 μm. This ASR can be reduced to 0.05 ohm-cm^2 by reducing the electrolyte thickness to 25 μm. The interfacial resistances can be reduced with further development (1) by decreasing the spacing between conductive particles in the electrodes, (2) by increasing the thickness of the electrodes, and (3) possibly by placing a mixed electronic/ionic conductor at the electrolyte/electrode interfaces. These developments are expected to reduce the ASR to closely approach the bulk resistance limit.

The performance of multi-cell MSOFC stacks is significantly less attractive than the performance of single cells. Figure 6 shows the improvement in the performance of multi-cell stacks since the operation of the first stack in January 1986. While the performance improvement has been dramatic, it must be improved further to equal that of the single cells. The improvement in open-circuit potential is a result of improvements in fabrication methods, particularly in matching the sintering shrinkages of the four different MSOFC materials.

The difference between single cell and multi-cell 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.

Future needs for development of the MSOFC include: (1) a more easily sinterable interconnect material, (2) cathode materials that are more stable at the sintering temperature, (3) development of ancillary materials such as insulation, manifolds, cements, and current collectors, (4) optimization of MSOFC designs for specific applications, (5) development of MSOFC systems, and (6) quality control development, including improved control of source materials and development of nondestructive analysis methods for the MSOFC structure.

CONCLUSIONS

The feasibility of the MSOFC concept has been proven, and the performance has been dramatically improved. The differences in thermal expansion coefficients and firing shrinkages among the fuel cell materials have been minimized, thus allowing successful fabrication of the MSOFC with few defects. The MSOFC shows excellent promise for development into a practical power source for many applications from stationary power, to automobile propulsion, to space pulsed power.

ACKNOWLEDGMENT

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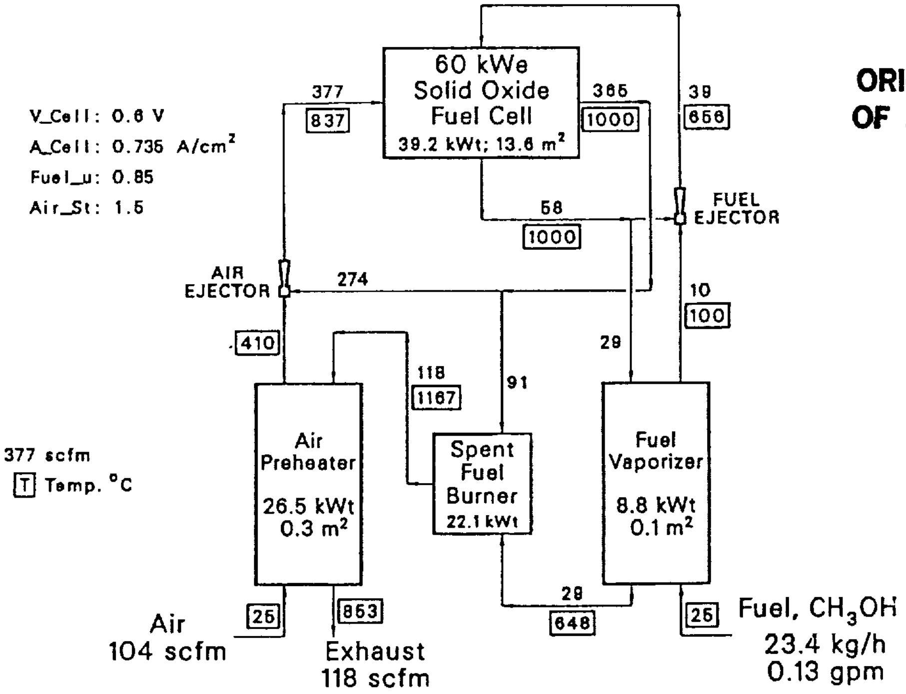


Figure 1. Methanol fueled MSOFC for vehicle propulsion.

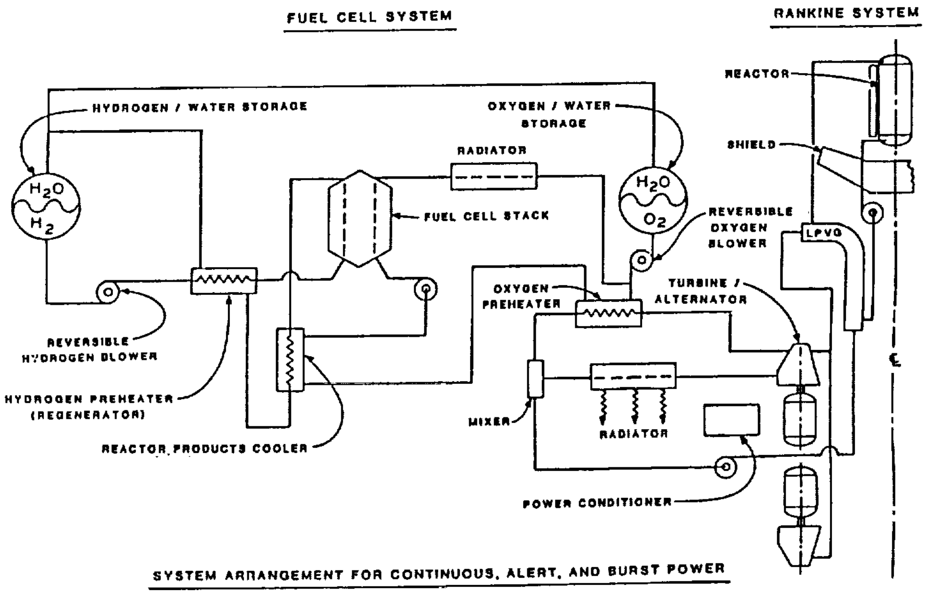
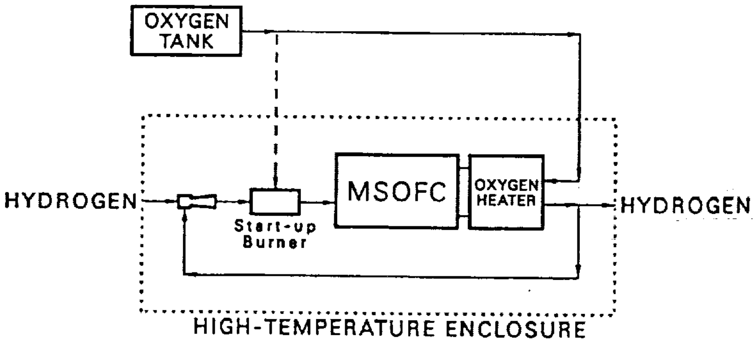


Figure 2. Space-based regenerative MSOFC system coupled with a nuclear reactor for pulse power.

The MSOFC Power System Is:
1) Simple in Design
2) All Solid State



Open-Cycle System Schematic

Figure 3. Simple open-cycle MSOFC system with no hydrogen regeneration and low fuel efficiency.

Monolithic Solid Oxide Fuel Cell
Open-Cycle System Power Densities
Can Exceed 4 kW/kg

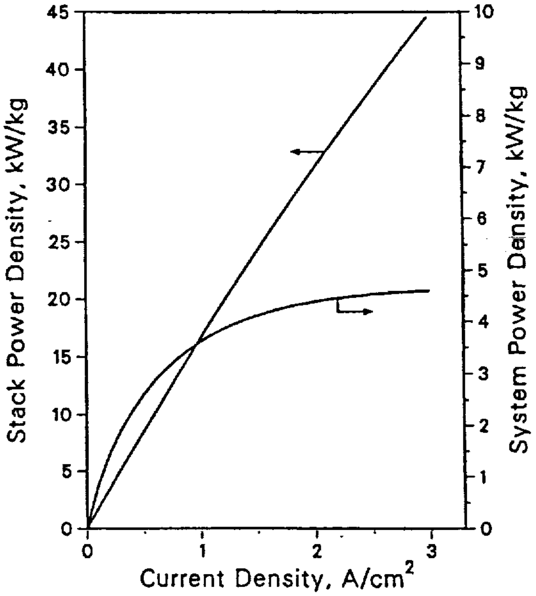


Figure 4. Stack and system power densities for a simple open-cycle space-based system.

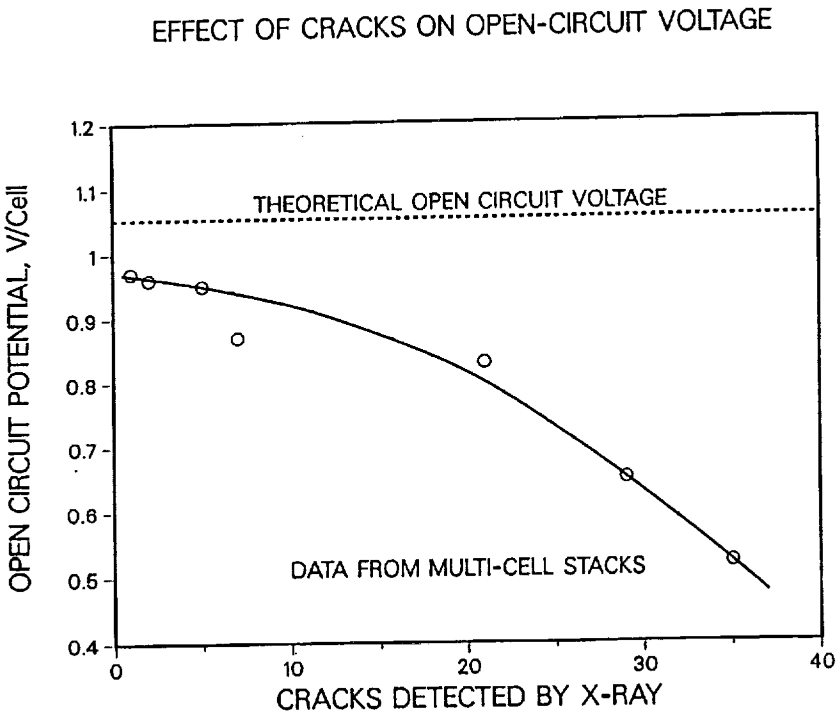


Figure 5. Improved MSOFC open-circuit voltage with reduction in ceramic defects.

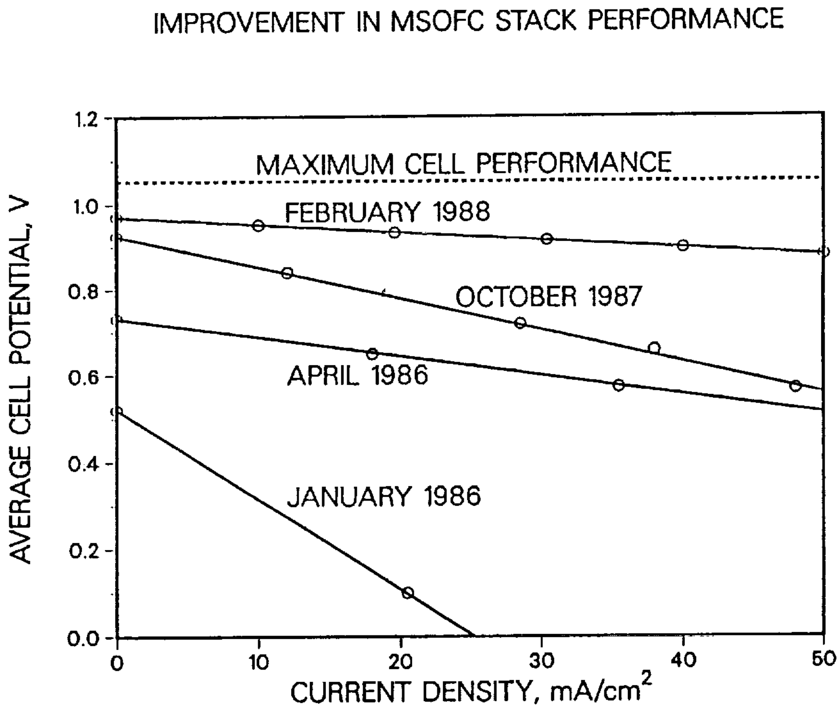


Figure 6. Improvement in multi-cell MSOFC stacks during development at Argonne.