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Advances in Tubular Solid Oxide Fuel Cell Technology

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ABSTRACT

This paper reviews the designs and performance of tubular solid oxide fuel cells (SOFCs). A large number of tubular cells of the porous support tube type have been electrically tested, some to times over 50,000 hours; these cells have shown excellent performance and performance stability. Since 1984, successfully larger electrical generators utilizing these cells have been built and operated; a 20 kW integrated SOFC system operated for 7064 hours during 1993-94. Results of development efforts to reduce cost and increase power output of tubular cells by eliminating porous support tube and increasing active length are described, and plans to utilize such air electrode supported cells in future SOFC systems are discussed.

INTRODUCTION

High temperature solid oxide fuel cells (SOFCs) utilizing zirconia-based electrolyte offer a clean, pollution-free technology to electrochemically generate electricity at high efficiencies. These fuel cells provide many advantages over traditional energy conversion systems; these include high efficiency, reliability, modularity, fuel adaptability, and very low levels of NOx and SOx emissions *(1,2)*. Furthermore, because of their high temperature of operation (~1000°C), these cells can be operated directly on natural gas eliminating the need for an expensive, external reformer system. These fuel cells also produce high quality exhaust heat which can be used either for process heat or a bottoming electric power cycle to further increase the overall efficiency. This paper reviews the advances in the tubular SOFCs made over the last few years.

POROUS SUPPORT TUBE (PST) TYPE TUBULAR CELLS

An SOFC essentially consists of two porous electrodes separated by a dense, oxygen ion conducting electrolyte. Oxygen supplied at the cathode (air electrode) reacts with incoming electrons from the external circuit to form oxygen ions, which migrate to

the anode (fuel electrode) through the oxygen ion conducting electrolyte. At the anode, oxygen ions combine with H_2 (and/or CO) in the fuel to form H_2O (and/or CO_2) and generate electricity. SOFCs of several different designs are presently under development; these include planar, monolithic and tubular geometries *(3,4)*. The materials being considered for cell components in these different designs are either same or very similar in nature. The most progress to date has been achieved with the tubular geometry fuel cell. Figure 1 illustrates the design of the original Westinghouse tubular geometry cell in which the active cell components are deposited in the form of thin layers on a porous ceramic support tube (PST). The materials for different cell components have been selected based on the following criteria:

(a) Suitable electrical properties required of different cell components to perform their intended cell functions.

(b) Chemical stability at high temperatures during cell operation as well as during cell fabrication.

(c) Minimum reactivity and interdiffusion among different cell components *(5)*.

(d) Matching thermal expansion among different cell components.

In addition to above materials selection criteria, the fabrication processes have been chosen so that every sequential component fabrication process does not affect those components already fabricated onto the support tube. The materials and fabrication processes used for different cell components have been discussed in detail previously *(4, 6)*; a summary is given in Table I. Development efforts to reduce the cost of the cells utilizing alternate fabrication techniques are currently in progress.

Table I - Cell Components, Materials, and Fabrication Processes

Component	Material	Fabrication Process
Support Tube	$ZrO_2(CaO)$	Extrusion-sintering
Air Electrode	Doped $LaMnO_3$	Slurry coat-sintering
Electrolyte	$ZrO_2(Y_2O_3)$	Electrochemical vapor deposition *(7, 8)*
Interconnection	Doped $LaCrO_3$	Electrochemical vapor deposition *(7, 9)*
Fuel Electrode	Ni-$ZrO_2(Y_2O_3)$	Slurry coat-electrochemical vapor deposition

The cell tube in all tubular cells is closed at one end. For cell operation, oxidant (air or oxygen) is introduced through a ceramic injector tube positioned inside the cell. The oxidant is discharged near the closed end of the cell and flows through the annular space formed by the cell and the coaxial injector tube. Fuel flows on the outside of the

cell from the closed end and is electrochemically oxidized while flowing to the open end of the cell generating electricity.

At the open end of the cell, the oxygen-depleted air exits the cell and is combusted with the partially depleted fuel. Typically, 50 to 90 percent of the fuel is utilized in the electrochemical cell reaction. Part of the depleted fuel is recirculated in the fuel stream and the rest combusted to preheat incoming air and/or fuel to the fuel cell. The exhaust gas from the fuel cell is at 600 to 900°C depending on the operating conditions and can be used in a cogeneration system for producing process steam or in a steam turbine bottoming unit for an all-electric system.

A large number of single SOFCs of the PST-type have been electrochemically tested at 875 to 1200°C, some to times over 50,000 hours, either on humidified hydrogen, a mixture of hydrogen and carbon monoxide, or natural gas. These cells have shown excellent performance and performance stability during long-term operation *(6, 10, 11)*. The voltage output of an early technology thin-wall PST-type cell over 50,000 hours is shown in Figure 2, which shows a degradation rate of less than 0.5% per 1000 hours. The voltage-current characteristics and power outputs of such cells have been discussed previously *(6)*.

AIR ELECTRODE-SUPPORTED TUBULAR CELLS

Increased power output per unit cell length is desirable to improve SOFC power plant economics. The earlier technology tubular SOFC, described above, was fabricated on a calcia-stabilized zirconia PST. Although sufficiently porous, this tube presented an inherent impedance to air flow toward air electrode. In order to reduce such impedance to air flow, the wall thickness of the PST was first decreased from the original 2 mm (the thick-wall PST) to 1.2 mm (the thin-wall PST). The calcia-stabilized zirconia support tube has now been completely eliminated and replaced by a 1.9 mm wall thickness doped-lanthanum manganite tube in the latest technology tubular SOFCs. This doped-lanthanum manganite tube is extruded and sintered to about 30 to 35 percent porosity, and serves as the air electrode onto which the other cell components are fabricated in thin layer form utilizing the same materials as for a cell with calcia-stabilized zirconia support tube. These latest technology tubular cells are designated as air electrode-supported (AE-supported) cells; schematic design of such a cell is shown in Figure 3.

The voltage output of an AE-supported cell (1.6 cm diameter, 50 cm active length) as a function of time at 1000°C and 450 mA/cm^2 current density, with 89% H_2 + 11% H_2O fuel (85% utilization) and air as oxidant (4 stoichs), is shown in Figure 4. The voltage shows excellent stability over time; such performance stability of AE-supported cells has now been confirmed for up to about 5000 hours.

The voltage-current characteristics of the AE-supported cells (1.6 cm diameter, 50 cm active length) at 900, 950, and 1000°C, with 89% H_2 + 11% H_2O fuel (89% fuel utilization) and air as oxidant (4 stoichs), are shown in Figure 5. These voltage-current characteristics at 1000°C are compared with those of the thick-wall PST and the thin-wall PST cells, under the same conditions, in Figure 6. The curves in Figure 6 clearly illustrate the significantly improved performance of the AE-supported cells over the PST-type cells. Elimination of one component (ceramic support tube) combined with the higher performance yields a lower cost SOFC ($/W) than the earlier technology PST-type cells.

In addition to eliminating the calcia-stabilized zirconia support tube, the active length of the cells has also been continually increased to increase the power output per cell. A greater cell power output decreases the number of cells required in a given power size generator and thus improves SOFC power plant economics. The active length has been increased from 30 cm for pre-1986 thick-wall PST cells to 150 cm for today's commercial prototype AE-supported cells. Additionally, the diameter of the tube in longer length AE-supported cells has been increased from 1.6 cm to 2.2 cm to accommodate larger pressure drops encountered in longer length cells. Figure 7 shows the power output from different cells illustrating the many-fold increase in power output from the latest technology AE-supported cells.

SOFC POWER GENERATION SYSTEMS

The basic design concept of the Westinghouse seal-less SOFC generator has been described previously *(4, 12, 13)*. This seal-less generator concept, illustrated in Figure 8, has been tested in a number of different-size generators, as summarized in Table II. In 1984, a 400 W generator consisting of two 12-cell bundles of 30 cm long thick-wall PST cells, connected in electrical series, was tested *(12, 13)* for about 2000 hours. During operation, this generator was cycled five times to approximately room temperature and back to operating temperature (about 1000°C). The successful test of this generator was followed by the design, construction, and test, in late 1986, of a larger 5 kW generator consisting of 324 cells of the same type *(13)*. This generator was tested for about 500 hours, and achieved 5.2 kW at 80 amperes with 6 stoichs air and 85% fuel (66.6% H_2, 22.2% CO and 11.1% H_2O) utilization at 1000°C.

Additional SOFC generators have been designed, built, and delivered for field testing by prospective customers of large-scale SOFC power generation systems. The Tennessee Valley Authority (TVA) acquired the first such unit for the purposes of demonstrating the capabilities of the technology and providing independent corroboration of overall performance and reliability. This 400 W generator, consisting of 24 thick-wall PST cells (30 cm long) arranged in two series connected bundles, was tested *(14, 15)* in early 1987 for about 1760 hours over a range of currents, fuel utilizations, air flows, and

Table II - Summary of Westinghouse SOFC Power Generation Systems

Customer	Size (kW)	No. of Cells	PST Type*	Cell Length (cm)	Test Time (hrs)	Year
U.S. DOE	0.4	24	Thick	30	2000	1984
U.S. DOE	5.0	324	Thick	30	500	1986
TVA	0.4	24	Thick	30	1760	1987
Tokyo Gas	3.0	144	Thick	36	5000	1987-88
Osaka Gas	3.0	144	Thick	36	3700	1987-88
GRI	3.0	144	Thick	36	5400	1989-90
U.S. DOE	20.0	576	Thin	50	3355	1990-91
The UTILITIES	20.0	576	Thin	50	7064	1992-94
JGU	20.0	576	Thin	50	817	1992
SCE	20.0	576	Thin	50	4500+	1994-95

*Thick: 2 mm wall thickness; Thin: 1.2 mm wall thickness.

temperatures, and demonstrated the capability of the system to satisfy its design requirements for automatic unattended operation and load follow.

Subsequently, Tokyo Gas and Osaka Gas each acquired a 3 kW SOFC generation system in 1987. Each system consisted of an SOFC generator module containing 144 cells, each 36 cm long of the thick-wall PST type, electrical air pre-heaters for generator temperature control, air and fuel handling systems, and a computer-based control system *(15)*. The generators could be run on hydrogen, a mixture of hydrogen and carbon monoxide, or the effluent from a customer supplied fuel gas supply such as a methane reformer. The testing and performance of these systems has been discussed in detail by Veyo *(15)*, Harada and Mori *(16)*, and Yamamoto, et al.*(17)*. In brief, each of these systems produced 3 kW of dc power as designed; the system at Tokyo Gas operated continuously and successfully for over six months. The system at Osaka Gas operated continuously for 3700 hours before being shut down for external (non-SOFC) causes.

In 1989, another 3 kW generator, again consisting of 144 cells of the same type, was fabricated to operate on desulfurized pipeline natural gas; this generator incorporated an integrated, internal reformer and partial recirculation of depleted fuel *(18)*. The generator was operated successfully for over 5400 hours, and either met or exceeded the design goals. This was the last generator to utilize the thick-wall PST cells.

In 1990, a 20 kW generator was fabricated. This generator consisted of 576 cells of 50 cm active length, now with the thin-wall (1.2 mm wall thickness) PST, and also incorporated an integrated, internal reformer and partial recirculation of depleted fuel. This generator was successfully operated for a total of 3355 hours on three different fuels - hydrogen, desulfurized pipeline natural gas, and naphtha - producing up to 20 kW *(19)*.

In 1992, a 25 kW dc power generation system, consisting of 1152 thin-wall PST cells of 50 cm active length, was fabricated and delivered for testing at Rokko Island, near Osaka, Japan, in a joint program with The UTILITIES, a consortium of The Kansai Electric Power Company, Osaka Gas Company, and Tokyo Gas Company. The cells in this generator were contained in two independently controlled and operated units. The detailed design and operation of this system have been discussed by Kusunoki, et al. *(20)* and Takeuchi, et al. *(21)*. One of the modules in this generator, rebuilt with the same type 50 cm active length thin-wall PST cells as the original module, operated for 7064 hours, setting a new record to date for operation time of a 20 kW class SOFC field unit *(21)*. Furthermore, this system was certified by the Ministry of International Trade and Industry (MITI) as being in compliance with all applicable regulations for a fossil-fueled power plant in Japan.

A second 25 kW SOFC system, a cogeneration unit supported by Osaka Gas Company and Tokyo Gas Company (known as JGU), was also fabricated and shipped to Japan during 1992 to produce ac power and intermediate pressure steam. The design and operation of this cogeneration system have been described by Shinozaki, et al. *(22)*; this system originally consisted of 1152 thin-wall PST cells of 50 cm active length in two modules. The cells in one of the two modules in this system are scheduled to be replaced during 1995 with the more advanced AE-supported cells of 1.6 cm diameter and 50 cm active length for further module testing.

In late May 1994, a 20 kW SOFC system, consisting of 576 thin-wall PST cells of 50 cm active length, was manufactured and delivered to the Highgrove Generating Station of Southern California Edison (SCE) in Grand Terrace (near San Bernardino), California. Leeper has described the characteristics and operation of this system *(23)*. In brief, this system is a packaged dc power generation system that includes the SOFC stack with integrated, internal reformers, an exhaust gas recovery heat exchanger (recuperator), an air supply system, a fuel supply system, a control module, and a data acquisition system. The unit was successfully started on June 7, 1994, and as of the end of 1994, has accumulated over 4500 hours of operation on desulfurized, pipeline natural gas. The maximum power output achieved to date has been 20.1 kW, with normal operation slightly in excess of 18 kW. The unit has also withstood three unplanned thermal cycles to room temperature so far, all caused by a variety of non-SOFC related reasons.

During 1995, an SOFC stack consisting of 576 advanced technology 1.6 cm diameter, 50 cm active length AE-supported cells will be installed in the above SCE system under a program with the Advanced Research Projects Agency (ARPA) of the U.S. Department of Defense. In addition to the new SOFC stack, a logistics fuel processor will be added that will enable the system to operate on diesel and jet fuels as well as on natural gas.

In addition, a 100 kW SOFC power generation system with the latest technology AE-supported cells is scheduled to be delivered to the Netherlands to a group of utilities consisting of the Dutch EDB consortium and the Danish ELSAM consortium. It will be installed at Duiven, near Arnhem, at a district heating system owned by NUON, one of the group of five Dutch gas and electricity distribution utilities which belong to the EDB consortium. The successful operation of this unit will represent a major milestone in the commercialization of advanced technology tubular SOFCs for large-scale power generation by the end of this decade.

SUMMARY

High temperature SOFCs based on yttria-stabilized zirconia electrolyte offer many advantages over traditional energy systems. These include high conversion efficiency, reliability, modularity, fuel adaptability, and virtually unlimited siteability due to very low NOx emissions. Furthermore, these cells produce high quality exhaust heat which can be used for process heat or a bottoming electric power cycle to further increase the overall plant efficiency. Westinghouse has developed the materials and fabrication processes for these fuel cells, increased the power output per cell many-fold over the last decade by eliminating the porous support tube and increasing the cell length, and has successfully employed and tested these cells for power generation in successively larger generators. When fully commercialized, the SOFC systems are expected to serve a wide range of power and heat applications, such as large-scale power generation by electric and gas utilities and industrial cogeneration.

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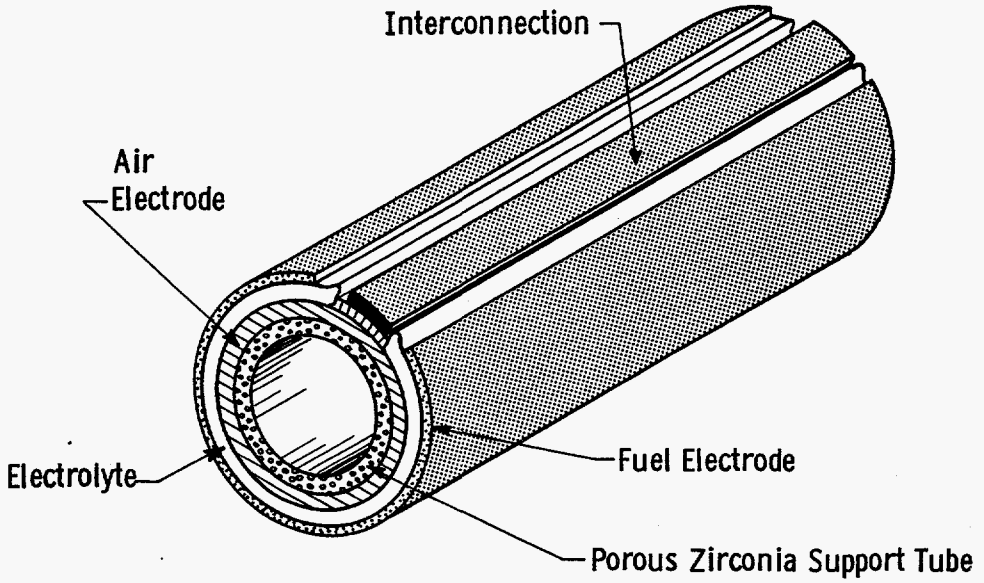

Figure 1 - Porous support tube (PST) type tubular solid oxide fuel cell design.

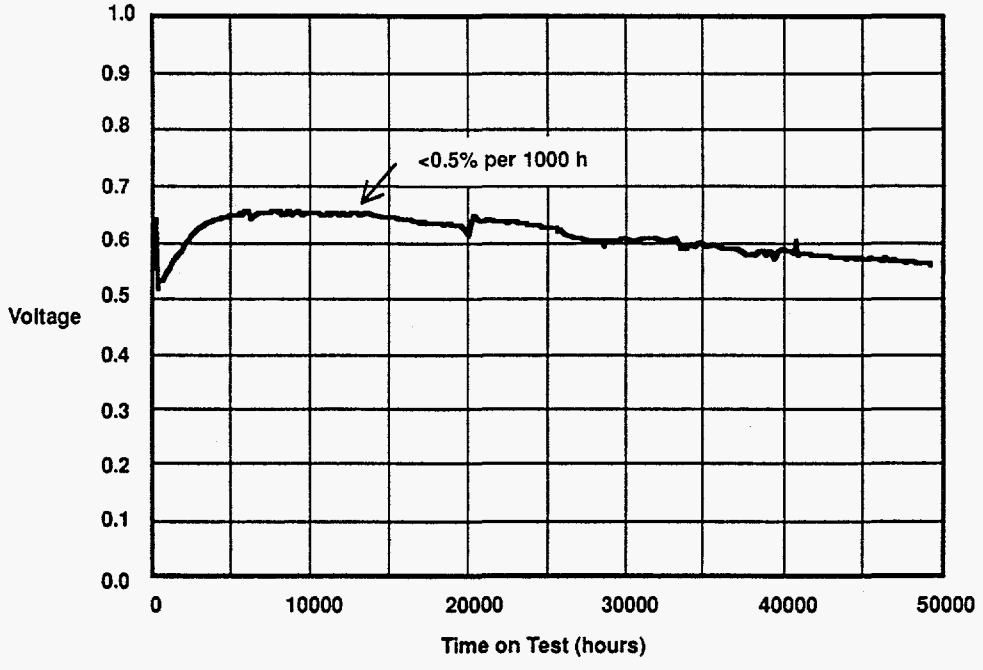

Figure 2 - Long-term test of an early technology thin-wall PST cell.

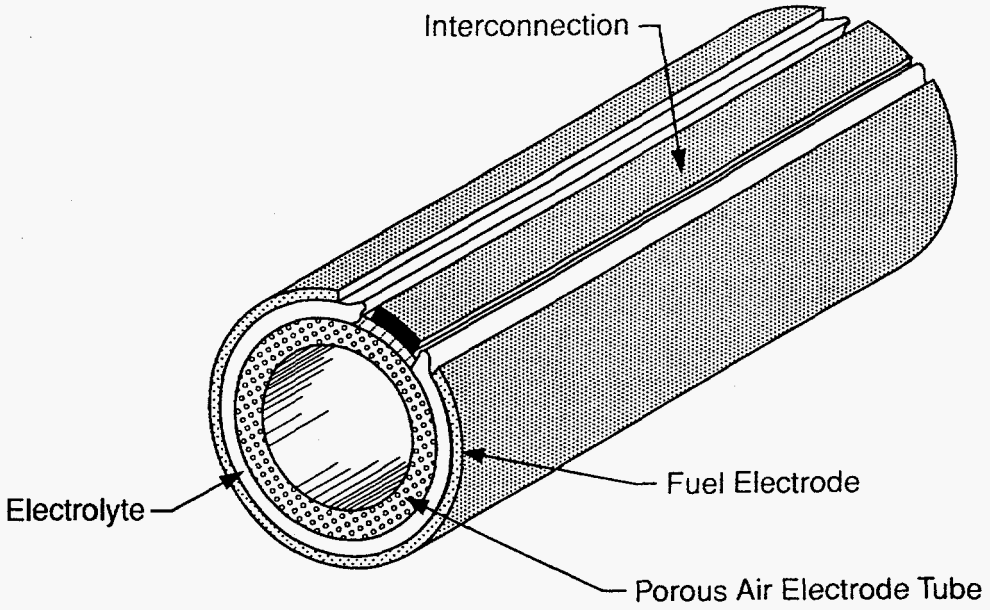

Figure 3 - Air electrode supported type tubular solid oxide fuel cell design.

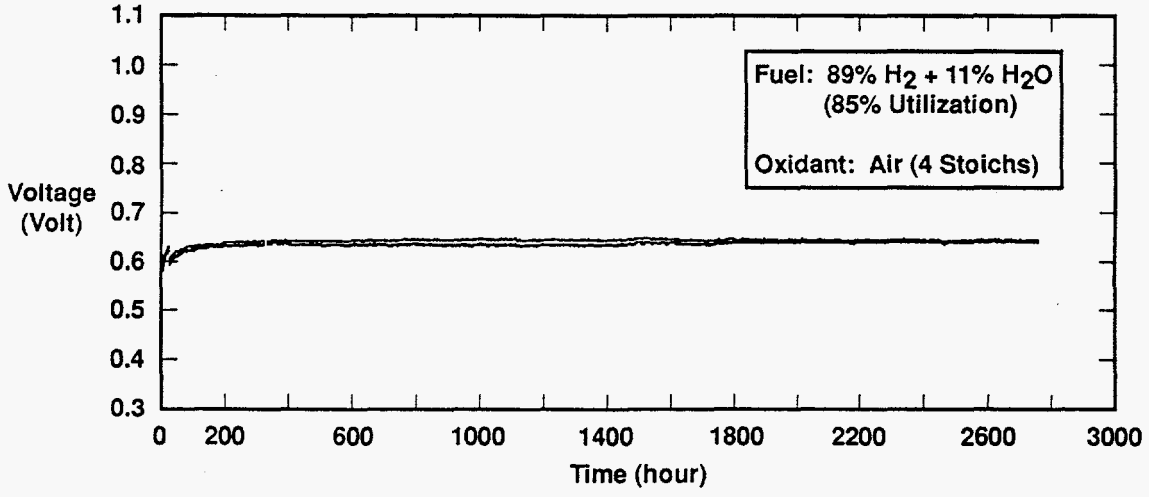

Figure 4 - Voltage stability of two AE-supported cells at 1000°C and 450 mA/cm^2.

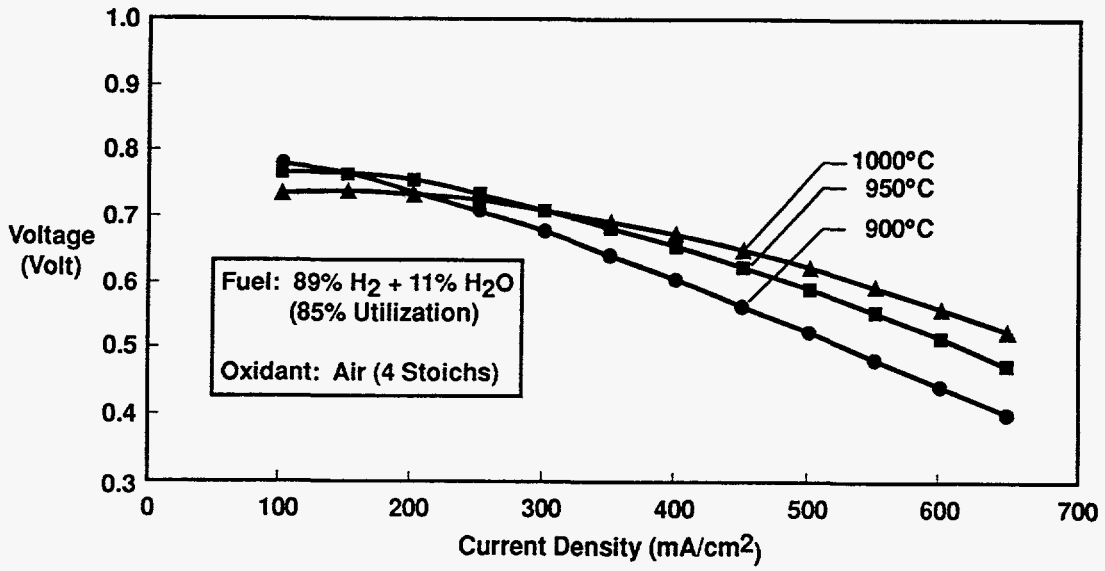

Figure 5 - Voltage-current characteristics of an AE-supported cell at different temperatures.

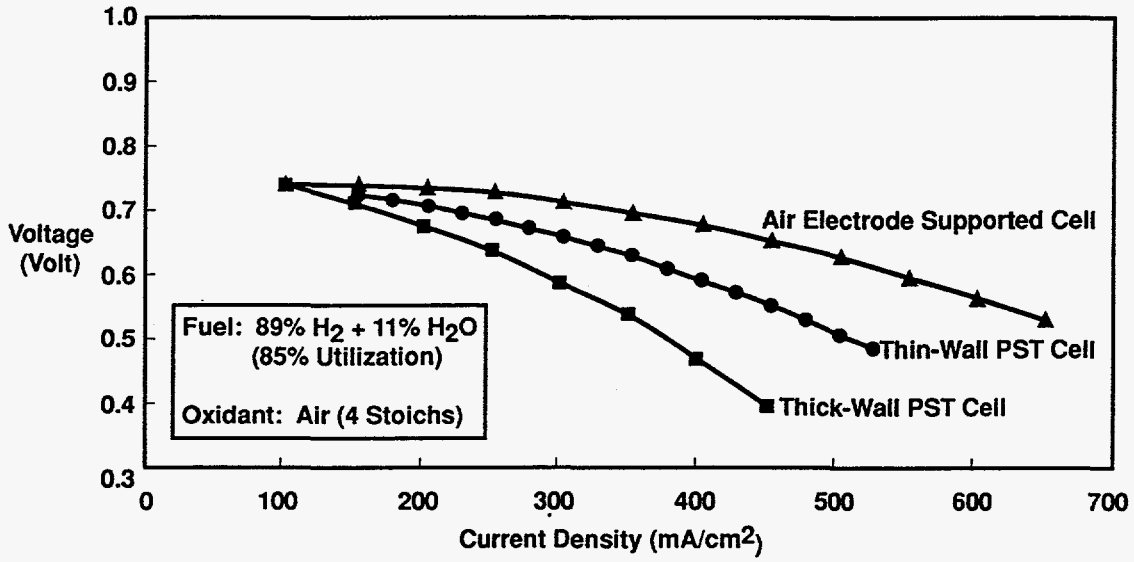

Figure 6 - A comparison of the voltage-current characteristics of the thick-wall PST, the thin-wall PST, and the AE-supported cells at 1000°C.

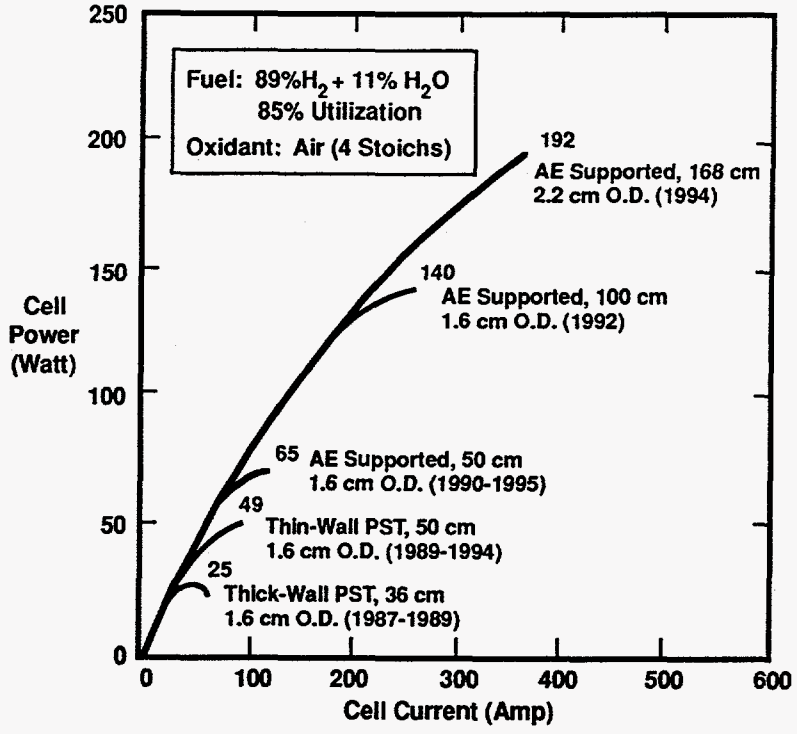

Figure 7 - Power output of different type and length cells.

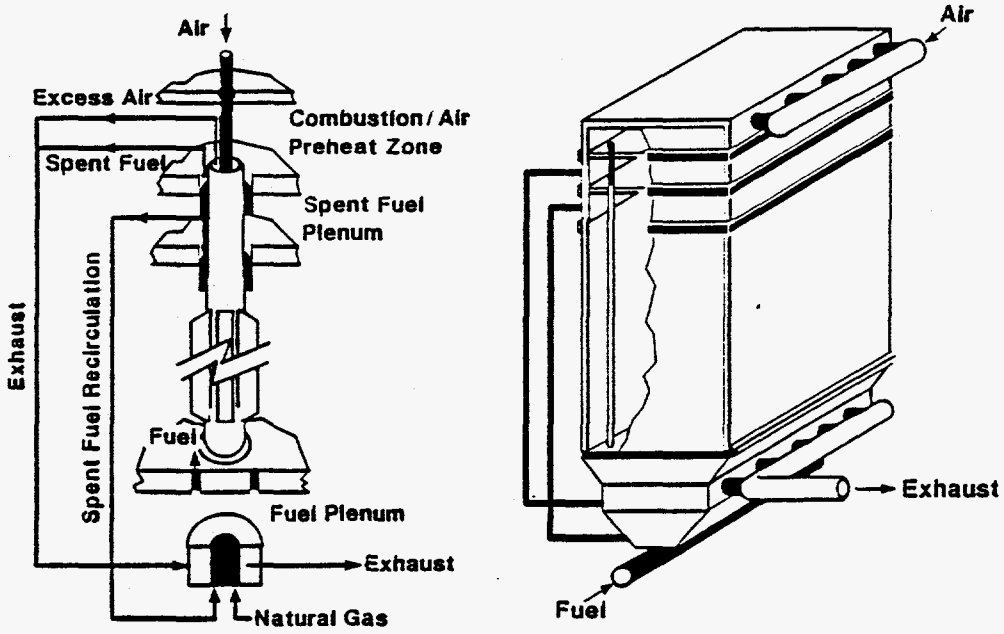

Figure 8 - Solid oxide fuel cell seal-less generator concept.