PROGRESS IN TUBULAR SOLID OXIDE FUEL CELL TECHNOLOGY

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ABSTRACT

This paper reviews the performance of the state-of-the-art solid oxide fuel cells that are fabricated using air electrode tubes, and discusses studies that are currently underway to reduce cell cost. A new design cell that combines the seal-less feature of tubular cells and a flattened air electrode with integral ribs is described; this design has a lower cell resistance and hence provides higher power output than tubular cells. Finally, the paper describes the operation of the 25 kW and 100 kW power generation systems that were built using such cells, and discusses the 250 kW pressurized SOFC-gas turbine hybrid system that is currently being built.

INTRODUCTION

The design, physical size, materials, and fabrication processes for the Siemens Westinghouse solid oxide fuel cells (SOFCs) have evolved over the last two decades. The current technology cells are fabricated using a doped lanthanum manganite tube (1). This tube is extruded and sintered to about 30 percent porosity and serves as the air electrode onto which other cell components are fabricated in thin layer form. Schematic design of such a cell is shown in Figure 1. The active length for today's commercial prototype cells is 150 cm with a diameter of 2.2 cm. The materials and fabrication processes for different cell components are summarized in Table I.

| Component       | Material          | Thickness | Fabrication Process       |
|-----------------|-------------------|-----------|---------------------------|
| Air Electrode Tube | Doped LaMnO₃ | 2.2 mm    | Extrusion-sintering       |
| Electrolyte     | ZrO₂(Y₂O₃)       | 40 μm     | EVD*                      |
| Interconnection | Doped LaCrO₃     | 85 μm     | Plasma spraying           |
| Fuel Electrode  | Ni-ZrO₂(Y₂O₃)    | 100 μm    | Slurry coat-EVD*          |

*EVD: Electrochemical Vapor Deposition (2).
CELL PERFORMANCE

Over three thousand tubular cells built using air electrode tubes have been electrically tested for up to about 25,000 h, either as single cells, in cell bundles, or in 25 kW and 100 kW SOFC power generation systems. Figure 2 shows the voltage-current characteristics from 800 to 1000°C for a 2.2 cm diameter, 150 cm length cell at 1 atm pressure using 89% H₂ + 11% H₂O fuel and air as oxidant. Such cells have performed well under a variety of operating conditions with less than 0.1% per 1000 h performance degradation. These cells have also shown the ability to be thermally cycled from 1000°C to room temperature over 100 times without any mechanical damage or electrical performance degradation.

The cells have also been found to tolerate small levels of air- and fuel-side impurities without any significant long-term performance problems. Presence of moisture in air results in only a slight decrease in voltage due to a small decrease in oxygen partial pressure. With sulfur dioxide (SO₂) impurity in air, no voltage losses have been observed at concentrations up to 2 ppm, which is about 14 times the U.S. Environmental Protection Agency (EPA) air quality limit. While operating with air containing seawater mist, some voltage losses occur but these can be entirely attributed to water vapor; most of the salt passes through the cell with only minimal deposition on the inside of the air electrode tube.

On the fuel side, addition of up to 5,000 ppm ammonia (NH₃) had no adverse effect on SOFC operation for up to 2,500 h of testing; ammonia actually acts as fuel increasing the cell voltage. The addition of 1 ppm HCl also did not have any detectable effect. However, the addition of 1 ppm H₂S to the fuel resulted in about 10% drop in cell voltage.
during the first 24 h and a declining slope in voltage versus time curve thereafter. On removal of H₂S from the fuel, most of the lost voltage was recovered indicating the deleterious effect of H₂S in the fuel to be reversible.

Figure 2. Voltage - Current Density Plots of a Typical 2.2 cm Diameter Cell at Various Temperatures.

INVESTIGATIONS TO FURTHER REDUCE CELL COST

Air Electrode Material

Over 90% of the weight of a tubular SOFC is that of the doped lanthanum manganite air electrode tube. Presently, the air electrode material is synthesized using high purity raw materials such as La₂(CO₃)₃ and MnO₂. Significant reduction in the cost of air electrode material is possible by the use of lower purity raw materials instead of pure lanthanum compounds in its synthesis. Air electrode material cost can also be reduced by utilizing compositions that have lower rare earth content. Use of such lower cost materials in fabricating air electrode tube has been successfully demonstrated by fabricating and electrically testing cells with these materials.

Fuel Electrode Deposition

Deposition of a Ni-yttria stabilized zirconia (YSZ) slurry over the YSZ electrolyte followed by sintering has also yielded fuel electrodes that are similar in electrical
conductive to those fabricated by the EVD process. Cells with sintered fuel electrodes have shown electrical performance equivalent to those with the EVD fuel electrodes. In fact, the sintered fuel electrode polarization is even lower than the already very low (7-15 mV) polarization for the EVD fuel electrodes. This is believed to be due to a larger contact area and a greater number of electrochemically active sites at the electrolyte/sintered fuel electrode interface. The fuel electrode sintering process has now been scaled up and implemented into cell manufacturing operations. All future cells will be manufactured using this process.

**Electrolyte Deposition**

The EVD process deposits uniformly thick (20 to 40 μm) gas-tight electrolyte film over the porous air electrode, reliably, uniformly, and in acceptable cycle time. Nonetheless, deposition of the electrolyte film by more cost-effective plasma spraying or a sintering process utilizing nanosize YSZ powders for slurry making and colloidal/electrophoretic technique for slurry deposition is also being investigated. If successful, this will result in further reduction in the cost of manufacturing tubular SOFCs.

**Alternate Geometry Cell**

To reduce the physical size and cost of SOFC generators, Siemens Westinghouse is presently investigating an alternate geometry higher power density SOFC. These cells combine all of the advantages of the tubular SOFCs, such as not requiring high temperature seals, while providing higher power per unit length and higher volumetric power density. This new design referred to as High Power Density Solid Oxide Fuel Cell (HPD-SOFC) has closed ends similar to the tubular design and provides integral air return paths that allow air to flow the entire length of the cell from the closed to the open end. The HPD-SOFC is flattened and incorporates ribs in the air electrode that act as bridges for current flow. Figure 3 compares the current path in a tubular SOFC and in a HPD-SOFC. The ribs reduce the current path length, which in turn reduces the internal resistance of the cell. The presence of the ribs, due to the decreased internal resistance of the cell, allows use of thinner air electrodes which in turn reduce air electrode polarization losses (a thicker air electrode results in a higher diffusion path for oxygen from the gas phase to the air electrode/electrolyte interface and thus results in higher polarization losses). The ribs also form air channels that eliminate the need for full length ceramic air injector tubes. A comparison of the air and the fuel delivery systems of the tubular SOFC versus the HPD-SOFC is shown in Figure 4. Shown in Figure 5 is a comparison of the theoretical and actual performances of a tubular SOFC and a HPD-SOFC on a stack volume basis. The higher performance of the HPD-SOFC on a stack volume basis results from the decreased resistance and tighter packing of the cells compared to the tubular SOFC. However, while the predicted peak power density for a HPD-SOFC is 0.43 W/cm³, the actual peak power density obtained so far in preliminary experiments has been 0.28 W/cm³. The difference between the predicted and the actual peak power density is thought to be due to the polarization losses at the air electrode/electrolyte interface. Work is currently underway to optimize the air electrode/electrolyte interface to decrease these polarization losses.
Figure 3. A Comparison of the Current Path in a Tubular SOFC and in a HPD-SOFC.
Figure 4. A Comparison of Air and Fuel Delivery in a Tubular SOFC and in a HPD-SOFC.
Figure 5. Comparison of Theoretical and Actual Performances for the Tubular SOFC and the HPD-SOFC on a Stack Volume Basis.

SOFC POWER GENERATION SYSTEMS

Siemens Westinghouse has designed, built and operated successively larger SOFC power generation systems since 1984. The design and operation of these systems have been described previously (3). Recent power generation systems fabricated with cells on air electrode tubes include two 25 kW systems and one 100 kW system. These are described below.

25 kW Atmospheric SOFC Systems

Each of the two 25 kW systems consisted of 576 50-cm active length cells (with EVD electrolyte, EVD fuel electrode, and plasma sprayed interconnection). One of these systems was operated at the Southern California Edison (SCE) Company’s Highgrove Generating Station (near San Bernardino), California, under a program with the U.S. Department of Defense’s Advanced Research Projects Agency (ARPA). This system also consisted of a logistic fuel processor, located outside the SOFC stack, enabling the system to be operated on either natural gas or on reformate from a logistic fuel such as DF-2 diesel or JP-8 jet turbine fuel. This system attained a total operating time of 5,582 h with 766 h on jet turbine fuel, 1,555 h on diesel fuel and 3,261 h on natural gas. The system endured five thermal cycles, produced up to 27 kW on each of the three fuels, and showed no evidence of performance degradation. After completion of the project, this system was restarted without any modification to the SOFC generator at the National Fuel Cell Research Center at the University of California, Irvine.
The other system, which was very similar to the one operated at SCE, was built for a consortium of Osaka Gas and Tokyo Gas, and completed 13,194 h of successful operation on desulfurized natural gas with a performance degradation rate of 0.1% per 1000 h. During this period, the system achieved 25 kW power output and sustained ten thermal cycles.

100 kW Atmospheric SOFC System

A 100 kW SOFC power generation system began operation in December 1997 in The Netherlands under a program with a consortium of Dutch and Danish utilities (EDB/ELSAM). The SOFC stack in this system contains 1,152 cells (2.2 cm diameter, 150 cm active length), which are arranged in twelve rows. Each row is composed of four cell bundles, each consisting of twenty-four cells arranged in rectangular array with three cells in electrical parallel and eight cells in electrical series. The cell rows are interconnected in serpentine fashion in electrical series. Between each cell row is an in-stack radiantly heated reformer. The thermal and hydraulic features of the 100 kW stack are shown in Figure 6. The stack is partitioned in elevation by porous baffles forming a fuel distribution plenum, an active cell zone, a spent fuel plenum, a combustion zone, and an air plenum. An ejector using pressurized desulfurized natural gas as the primary fluid is used to extract a portion of the spent fuel and mix it with fresh fuel before the mixture is introduced into an adiabatic pre-reformer where the higher hydrocarbons are reformed. From the pre-reformer, the predominantly methane stream is routed to the top of the in-stack reformers. The mixture flows downward through catalyst material before exiting within the fuel plenum at the bottom of the stack. The completely reformed fuel flows upward within the stack along the exterior of cells where it is electrochemically oxidized. The stack exhaust gas departs at the combustion zone temperature, approximately 850°C. The stack is cooled with process air which enters the stack at approximately 600°C. The thermally and hydraulically integrated reformer requires no external source of water during normal operation.

The 100 kW SOFC power system is composed of three primary assemblies or “skids” plus a power conditioner skid and an SOFC exhaust gas warmed hot water heater skid. The generator (stack) skid, the thermal management skid, and the fuel supply system skid comprise the three primary assemblies. These are shown in Figure 7.

The system passed a customer-witnessed factory acceptance test at Siemens Westinghouse facilities in Pittsburgh, Pennsylvania in October 1997 during which it generated electric power for 335 h before shutdown on October 30. The unit was subsequently separated into its constituent skids, suitably crated and shipped via overland truck and air freight to the test site near Arnhem, The Netherlands. The unit was installed and reconnected in the latter half of November and restarted in early December 1997. The unit was officially accepted by the EDB/ELSAM on February 6, 1998 after successfully completing a site acceptance test. This system has been AGA certified by International Approval Services as in compliance with the proposed harmonized Fuel Cell Power Plant Standard Z21.83.CGA12.10. In addition, it has been designed and constructed to conform with applicable Dutch and European Directives (codes and standards) and qualified for the “CE” mark.
Figure 6. Thermal and Hydraulic Features of the 100 kW SOFC Stack.

Figure 7. EDB/ELSAM 100 kW SOFC System.
The system achieved an electrical generation efficiency of 43% (net ac/LHV), using Dutch pipeline natural gas fuel at a net system output of 106 kWe ac to the grid. Nominal operating conditions are 1000°C and 80% fuel utilization. Emissions measurements confirmed a NOx level less than 0.2 ppmv with undetectable levels of SOx, CO, and unburned hydrocarbons. A plot of system performance over 4,035 hours of operation is shown in Figure 8. System operation was suspended at the end of June 1998 because internal voltage measurements indicated an accelerating voltage decline in a segment of the stack. Open circuit behavior upon shutdown showed good cell voltage, hence healthy cells, thereby indicating excessive stack resistance. During cool-down, stack voltages universally dropped to the nickel oxidation potential. The generator module skid was removed from the site in July 1998 and shipped to Siemens Westinghouse facilities in Pittsburgh for inspection and repair. Disassembly revealed that the baffle separating the combustion zone from the spent fuel plenum had broken in several places permitting air to enter the spent fuel plenum. This would consume fuel yielding stack operation at much higher fuel utilization than nominal, thus explaining to a great extent why the observed electrical efficiency was lower than the expected 47%. This broken baffle also would explain the low cell voltage observed during cooldown. Further disassembly revealed significant areas of nickel felt separation from cell interconnections at the end of bundles, especially near the end of bundle rows. This felt separation significantly increased the stack internal impedance with concomitant detrimental impact upon system generation efficiency. In addition, five cells, each located at the end of a bundle row, were found to be cracked. Nickel felt separation from interconnections is believed to be related to quality issues in cell manufacture and bundle assembly coupled with excessive mechanical loads at the end of bundle rows. The reason for the cracked cells is believed to be related to mechanical loads associated with the end of row current strap. Design improvements yielding a more robust baffle and reduced mechanical loading of the cells have now been implemented, the stack rebuilt and restarted in early 1999. The rebuilt stack has now operated for over 1200 h (as of May 1999) providing up to 108 kW ac to the Dutch grid at an efficiency of 45%; a plot of system performance since stack rebuild is shown in Figure 9.

250 kW Pressurized SOFC-Gas Turbine Hybrid System

All systems described above have been operated at 1 atm pressure. Operation at elevated pressures yields a higher cell voltage at any current density due to increased Nernst potential and reduced cathode polarization (1), and thereby permits higher stack efficiency and greater power output. With pressurized operation, SOFCs can be successfully used as replacements for combustors in gas turbines; such SOFC-gas turbine hybrid power systems are calculated to reach efficiencies approaching 70%. Siemens Westinghouse, under the sponsorship of Edison Technology Solutions, is currently fabricating a 250 kW class pressurized SOFC-gas turbine hybrid power system for proof-of-concept testing. The SOFC module (1,152 cells of 2.2 cm diameter and 150 cm length) of the hybrid system will produce approximately 200 kW of power operating at 3.5 atm pressure and the gas turbine about 50 kW. The efficiency of the power system is expected to be about 57% (based on LHV) running on desulfurized natural gas.

The system configuration, illustrated in Figure 10, employs a two-shaft gas turbine and uses a pressurized SOFC stack upstream of the gas turbine combustor. Process air is
Figure 8. 100 kWe SOFC Generator Terminal Voltage, Current and Power (Before Stack Rebuild).

Figure 9. 100 kWe SOFC Generator Terminal Voltage, Current and Power (After Stack Rebuild).
compressed before being introduced to the pressurized SOFC stack. The stack produces dc electricity and generates a high pressure, high temperature exhaust gas (850°C). This high pressure exhaust is passed through the first turbine stage driving the compressor and then expands through a power turbine connected to an ac alternator. The power turbine exhaust is ducted through a recuperator to heat incoming process air.

A schematic of the pressurized SOFC/gas turbine hybrid system is shown in Figure 11. The system will be installed at the National Fuel Cell Research Center on the University of California at Irvine campus, and is expected to begin operation near the end of 1999.

SUMMARY

Siemens Westinghouse tubular cells built using air electrode tubes exhibit excellent electrical performance, performance stability, reliability, and ability to sustain thermal cycles. This has been confirmed by successful operation of two 25 kW and one 100 kW power generation systems built employing such cells. In addition, significant cost reductions are being achieved by adopting lower cost materials and non-EVD processes in cell production. Scale-up of the technology to 250 kW size systems and beyond is now underway.
Acknowledgments

The author acknowledges the contributions of his many colleagues whose work is reviewed in this paper. The development of the SOFC technology has been supported by the U.S. Department of Energy (DOE), the Gas Research Institute (GRI), and various utility and commercial sources. The pressurized SOFC testing effort is supported by Ontario Power Technologies and its Canadian funding partners, and New Energy Development Organization (NEDO) of Japan and its participating electric power companies.

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