DIRECT OXIDATION AS A MARKET ENabler FOR SOLID OXIDE FUEL CELLS

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ABSTRACT

Direct oxidation for solid oxide fuel cells (SOFCs) is a technology that enables the SOFC to oxidize dry hydrocarbon fuels directly in the anode without any fuel reforming. Researchers from the University of Pennsylvania’s Department of Chemical and Biomolecular Engineering have achieved significant advances in direct oxidation utilizing a Cu/CeO2/YSZ anode. This technology has been licensed exclusively by Franklin Fuel Cells, Inc. of Wayne, Pennsylvania, for the purpose of commercializing SOFC stacks capable of operating on a variety of hydrocarbon fuels. In this paper, we describe the development effort underway at Franklin Fuel Cells Inc. in the area of direct oxidation SOFC stacks and the potential for this technology to propel SOFC product commercialization.

INTRODUCTION

Fuel cells elude mass commercialization for many well-known factors. Chief among these is the difficulty in establishing a supply infrastructure for hydrogen, the fuel cell’s fuel of choice, without evidence of a significant demand for hydrogen from an existing fuel cell fleet and a consumer market unwilling to accept fuel cells without an existing hydrogen supply network. The availability of fuel flexible fuel cell devices, ones capable of operating on readily available fuels such as natural gas, gasoline or diesel, can help bridge this gap between supply and demand, enabling fuel cells to penetrate markets unlikely to have access to hydrogen for many years.

The direct oxidation technology developed at the University of Pennsylvania (Penn) for solid oxide fuel cells (SOFCs) is one that enables the SOFC to oxidize dry hydrocarbon fuels directly in the anode without any fuel reforming (1-3). This technology has been licensed exclusively by Franklin Fuel Cells (FFC), Inc., of Wayne, Pennsylvania, for the
purpose of commercializing SOFC stacks capable of operating on a variety of fuels. The technology employs a composite anode of Cu/\text{CeO}_2/\text{YSZ}. Conventional SOFCs utilize a composite of Ni and yttria-stabilized zirconia (YSZ) in the anode. Although Ni has been shown to be an excellent catalyst for the oxidation of hydrogen and has good electrical conductivity, its presence does not allow for the use of dry hydrocarbon fuels. Above 600°C, Ni catalyzes the formation of graphite from dry hydrocarbons, which can quickly deactivate the cell due to carbon deposition (4,5). On the other hand, Cu is an excellent electronic conductor and relatively inert for the formation of the C-C bond, so it will not form carbon deposits in the presence of dry hydrocarbons. Ceria is added to the anode because of its high activity for hydrocarbon oxidation and high ionic conductivity.

Single cells utilizing the Cu/\text{CeO}_2/\text{YSZ} anode, a dense 60 μm YSZ electrolyte and a 50/50 YSZ/LSM cathode have demonstrated performance at 700°C of 0.150 to 0.250 W/cm² with dry hydrocarbon as well as pure hydrogen for fuel. These cells have also demonstrated stable power generation using hydrocarbon fuels having sulfur levels similar to that in gasoline.

With no need for external or internal fuel reforming, simpler fuel conditioning if at all, no precious metals, and utilizing high yield, low cost manufacturing methods, this proprietary technology has the potential to dramatically simplify the fuel cell system drastically reducing its cost while improving efficiency. Fuel flexibility, lower $/kW, and a simpler, more reliable system design mean less time to market.

**MARKET POTENTIAL**

The market for stationary and portable fuel cells is estimated to be as much as $6.5 billion by 2010. Two segments of particular interest are distributed generation and mobile applications. Exponential growth in microprocessor-based systems is expected to result in increases in overall demand for electricity potentially exceeding 3% year over year. Additionally, these systems demand very high quality and reliable power. The distributed generation equipment market is roughly $5 billion today and is expected to grow between 15% and 25% per year. The world wide automotive market represents a 4.1 GW per year market with 2% to 3% yearly growth. Auxiliary power units for passenger cars and trucks alone could represent a 0.3 GW per year market by 2010.

The top challenges currently preventing fuel cells from penetrating these markets include cost, reliability and fuel availability. Packaged systems utilizing fuel cell generators are currently priced in the thousands of dollars per kilowatt. In order for mass commercialization of fuel cells to occur, the cost of these systems must come down drastically. Additionally, customer acceptance of fuel cells will not likely happen unless the fuel cell inside is invisible to the user. That is, the reliability and durability of the fuel cell systems must be at least as good as that of the incumbent product. Lastly, the fuel infrastructure for hydrogen needs to be in place. Issues of customer acceptance for devices that store hydrogen, especially at very high pressures, are also of concern.

A solution to the problem of fuel availability has been the use of a fuel reformer to produce hydrogen from readily available hydrocarbon fuels such as natural gas, methanol, gasoline and diesel. Reformer technology, however, is not yet mature, and
reforming systems add cost, reduce efficiency and performance, and lower the reliability of the fuel cell system.

The technology under development at Franklin Fuel Cells addresses the fuel availability and reformer performance issues by eliminating the need for fuel reformation, external or internal to the cell, for operation using dry hydrocarbon fuels. This technology also reduces the need for sulphur removal, greatly simplifying or eliminating the need for fuel conditioning. With a much simpler balance of plant and more efficient cell operation, due to the elimination of the reforming stage, the SOFC system can be manufactured with a significant cost, performance and reliability advantage.

ADVANCES AT THE UNIVERSITY OF PENNSYLVANIA

It is well known from the literature on catalytic, steam reforming that Ni catalyzes the formation of graphite fibers, even under conditions in which thermodynamics would predict that the material should be stable towards carbon formation (4,5). Efforts at the University of Pennsylvania have focused on developing anodes based on Cu cerments, since Cu is an excellent electronic conductor but is catalytically inert for the formation of carbon fibers (1-3). However, because of the low melting temperatures of CuO and Cu2O, it was necessary to develop alternative fabrication procedures to replace the conventional ceramic processing methods.

The method developed at Penn involves preparing a highly porous YSZ matrix, impregnating this matrix with aqueous solutions of Cu(NO3)3, then calcining above 450°C to decompose the nitrate and form the oxide. While various methods can be used to make the porous matrix, a method that lends itself to the fabrication of thin electrolytes and anode-supported cells involves dual tape casting of YSZ, with one layer containing pore formers (6,7). With the appropriate choice of conditions, we have prepared YSZ wafers with a thin dense layer supported by porous YSZ having porosities as high as 80% after calcination to 1550°C (8). While Cu-YSZ cerments are stable in hydrocarbon fuels, the performance of these anodes is poor unless CeO2 is added, again by impregnation of aqueous solutions of Ce(NO3)3. While ceria probably plays multiple roles in the direct-oxidation anodes, providing catalytic activity for hydrocarbon oxidation appears to be at least one of those roles (9).

The Cu/CeO2/YSZ anodes have been tested and shown to be stable for a wide variety of fuels, including some that are liquids at room temperature (10). For pure CH4 at 800°C, carbon formation was shown to be negligible, even after 1000 hrs. For larger hydrocarbons, free-radical, gas-phase reactions can lead to fouling of the anode under some conditions; but deactivation is reversible upon re-oxidation of the anode (10). The Cu/CeO2/YSZ anodes are also reasonably resistant to sulfur poisoning (11). In the presence of sulfur-containing fuels, deactivation is due to reaction of CeO2 to Ce2O2S and deactivation is again reversible upon treating the anode in steam. Thermodynamic analysis suggests that the Cu/CeO2/YSZ anodes should be stable in fuels that contain 100 ppm sulfur (12).
DEVELOPMENT EFFORTS AT FRANKLIN FUEL CELLS

With exclusive license to intellectual property developed at the University of Pennsylvania and with enabling patents contributed by the Gas Research Institute (GRI), Franklin Fuel Cells is engaged in its initial phase of product development. The focus of its present work is development of prototype SOFC multi-cell stacks capable of the direct oxidation of hydrocarbon fuels. To carry out the work, FFC has partnered with the Sarnoff Corporation, of Princeton, New Jersey. This work involves four key areas: transfer of technology from Penn to FFC, scale up of cell design and fabrication process, design and development of stack technology, including glass sealing, and testing and characterization of stack performance.

Penn’s copper anode button cells served as the starting point, and FFC development began with the successful demonstration of Penn-style single cell performance at the Sarnoff labs. Figure 1 provides a V-I curve typical of Penn-style cells fabricated and tested at the Sarnoff lab. As shown in Figure 1, the power density of the cell is 251 mW/cm², 177 mW/cm², and 181 mW/cm², at 715°C, using hydrogen, propane and butane as fuel, respectively. The cell has the similar microstructure as Penn’s cell as well.

![Figure 1. Button cell performance demonstrated at Sarnoff using Penn's process.](image-url)

The next phase in development, cell scale-up, involved modifying the tape casting process for larger (100 cm² active area) cell fabrication. This task includes modifications to the slurry processing, adjustment to formulation, cell sintering profile development as well as development of the cathode application process. The major challenges here are creating defect-free, uniform, ceramic green tapes and producing flat cell disks. 10 cm x 10 cm flat cell disks have been successfully manufactured. Validation tests using button cells made by the modified process show higher power density than the standard cells made by the original process. The new process has increased the manufacturing batch size by many multiples, compared to the process developed at Penn, and reduced defect rates by 70 to 80% in key areas. Ongoing work is aimed at further characterization of...
process critical parameters, the adoption of necessary process controls, and further reductions in manufacturing cycle times.

A crystallizing glass, designed at Sarnoff, will be used to achieve a gas-tight seal between the cell disk and the interconnect. This glass was selected out of more than 40 candidate glasses, based on the adhesion to cell disk and interconnect, wetting behavior, thermal expansion, and other criterions. The selected glass is mechanically and chemically stable in both air and hydrocarbon fuel at the cell stack operating temperature. Compatibility of the glass with the cell and interconnect in terms of thermal expansion and wetting are the most critical factors for the reliability of the seal during the operation as well as during heat-up and cool-down cycles. The glass seal is designed to have long-term stability at the fuel cell’s operating temperature.

FFC’s initial technology demonstration involves the design and fabrication of a direct oxidation SOFC stack capable of producing between 100 and 250 watts on a variety of dry hydrocarbon fuels. Designed for operation at 700 to 750°C, the stack is internally manifolded and uses a metal alloy for interconnect material. The interconnect material is selected and treated to possess high mechanical and chemical stability at the stack operating temperature and to closely match its thermal expansion to that of the cell. Glass seals provide cell-to-interconnect bonds, mechanical integrity to the stack, and air/fuel isolation. Precise thermo-mechanical compatibility among the cell, interconnect, and the sealing glass is a crucial design element of the stack. The stack design also features compliant low-resistance electrode contacts. Uniform gas flow over the electrodes is achieved by means of a proprietary electrode contact design. This design allows turbulent gas flow without significant pressure drop from the inlet manifold to the exit manifold. Materials in the fuel flow path are selected and treated to possess high stability in the fuel gas atmosphere at the stack operating temperature.

**CONCLUSIONS**

Direct oxidation solid oxide fuel cells enable drastic cost, performance and reliability improvements in the fuel cell system, while providing for the flexibility to use readily available fuels like natural gas, propane, gasoline and diesel. A new company, Franklin Fuel Cells, has been founded in order to commercialize the direct oxidation technology developed at the University of Pennsylvania. This technology utilizes copper-based anodes in a medium temperature SOFC system, requires no precious metals, and is easily manufactured using proven, inexpensive methods.

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