ADVANCED PLANAR SOLID OXIDE FUEL CELL: DESIGN CONCEPT AND FABRICATION METHODOLOGIES

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ABSTRACT

Babcock & Wilcox has initiated a multiple phase program to develop a high-performance planar solid oxide fuel cell (SOFC). A multidisciplinary team has been established to conduct the Phase I effort - Concept Feasibility Demonstration. A key focus of the B&W program is SOFC stack manufacturability and reliability. This paper presents the current design concept and the chosen fabrication methodologies.

INTRODUCTION

High temperature fuel cell systems offer unsurpassed potential for clean, economic power generation. Solid oxide fuel cells (SOFCs), in particular, exhibit several attractive features, such as (1) high electrical efficiency and the possibility of enhancing overall cycle efficiency through the use of the high-grade waste heat for power generation or industrial processes; (2) very low levels of environmental pollutants; (3) the ability to utilize a wide range of fuels, including hydrogen, natural gas, vaporized hydrocarbons, and coal gas; and (4) flexibility in the planning and siting of power generation capacity as a result of the modular nature of fuel cell units. Planar configuration SOFCs exhibit an additional key characteristic of high power density.

Solid oxide fuel cells have been under development for over 20 years, and in this period a number of basic design concepts have been considered. Westinghouse and ABB were early pioneers in SOFC development and made significant progress in developing the key constituent materials; they also focussed these early efforts on
tubular cell designs. Although Westinghouse has continued to pursue tubular SOFCs, ABB terminated their effort, as they believed that the tubular design and the associated high costs of manufacturing would severely limit commercialization [1]. Argonne National Laboratory [2] and Allied-Signal [3] have expended significant effort over the past 5 years developing the monolithic planar design, but have shown limited success. Finally, numerous organizations have been investigating a wide range of additional planar SOFC concepts, focusing on different interconnect (and gas manifolding) designs and a range of fabrication methodologies.

Given the attractive features of planar SOFCs, it is clear that they have tremendous potential in a broad range of industrial, commercial and military applications. However, the key to successful commercialization of SOFCs will be the ability to manufacture reliable, low-cost power modules of the appropriate sizes. Although many SOFC concepts have been successfully demonstrated at the lab scale, subsequent scale-up of the manufacturing processes and commercialization have been difficult. For example, performance characteristics exhibited by single planar cells and small stacks have not been achieved in larger stacks.

In 1991, B&W conducted an extensive evaluation of fuel cell technologies, focusing primarily on SOFCs. B&W concluded that the tubular SOFC design was unattractive due to low power densities and high manufacturing costs. It was also concluded that the monolithic fuel cell concept, although in principle very attractive, was not a viable option - co-firing the complete cell stack does not appear to be possible. As a result of this study, B&W initiated a multiphase program to develop an advanced planar SOFC. Given that B&W is getting a late start in this technology, it is essential that we access the best capabilities available in the U.S. Thus, we are establishing an industry led team comprising B&W, National Laboratories (Idaho National Energy Laboratory - INEL and Argonne National Laboratory - ANL) and universities (University of Missouri-Rolla and Northwestern University's Basic Industrial Research Laboratory - BIRL).

Phase I of the B&W Program, started in early 1992, is directed at demonstrating the feasibility of the advanced planar concept and will last 2 years. This paper presents the basic design concept and fabrication approaches being pursued by the B&W Team in Phase I. Initial results of our development efforts will also be reviewed.

CONCEPTUAL DESIGN AND FABRICATION METHODOLOGIES

The advanced planar SOFC concept under development in Phase I of the B&W Program is illustrated in Figure 1. The materials of construction and selected physical parameters are given in Table I.
TABLE I
SOFC Materials and Physical Parameters

| LAYER    | MATERIAL                  | THICKNESS       | DENSITY  |
|----------|---------------------------|-----------------|----------|
| Interconnect | La$_{x}$Ca$_{1-x}$Cr$_{y}$Co$_{1-y}$O$_3$ | 0.050-0.065"   | > 95%    |
| Cathode  | La$_{x}$Sr$_{1-x}$MnO$_3$      | 0.015-0.020"   | 50-70%   |
| Electrolyte | 8 m/o Y$_2$O$_3$-ZrO$_2$  | 0.001-0.002"   | > 94%    |
| Anode    | Ni/ZrO$_2$ Cermet (30-45% Ni) | 0.004-0.008"  | 40-60%   |

The constituent materials chosen for this work are essentially the same as those commonly used for SOFCs, with the exception of the chromite interconnect. These materials have been shown to be relatively compatible with each other and stable under SOFC operating conditions. By appropriately adjusting the cation composition, these materials also have thermal expansion coefficients which are sufficiently close to that of the stabilized zirconia; this is an important consideration in minimizing internal stresses. The La$_{x}$Ca$_{1-x}$Cr$_{y}$Co$_{1-y}$O$_3$ interconnect material is a recently developed composition which is readily sintered in air at 1350-1500°C and appears to have superior stability and electrical properties when compared to previous chromite materials [4,5].

The Phase I design is based on a cross-flow configuration in which the gas distribution channels are formed within the interconnect plates. The interconnect plates will be the primary load-bearing elements within the stacks and thus will be on the order of 0.050 to 0.065" thick. A dry pressing and sintering process was chosen for Phase I fabrication of 2-4 inch square plates; densities greater than 95% of theoretical are required to properly separate the fuel gas and air. After sintering, the plates are creep flattened and the grooves are formed by machining. Although B&W does not envision this approach to be optimal for manufacturing, it appears to be the most direct method to pursue in this feasibility demonstration project.

In fabrication of the anode-electrolyte-cathode "trilayer", B&W had three different approaches to choose from: (1) forming a thin zirconia sheet by slip casting or tape casting and sintering, followed by deposition of the appropriate electrodes on each face - for example see references [1,6-9]; (2) forming a green trilayer structure using extrusion or tape casting methods and then co-sintering the layers - for example see references [2,3,10,11]; or (3) using appropriate methods to sequentially deposit the cathode, electrolyte and anode layers onto an interconnect plate - for example see references [12,13]. The B&W team chose to pursue the sequential deposition...
approach because it should allow the fabrication of a thin electrolyte layer - a key objective in our design. This approach also eliminates the potential for defects and stresses in the electrolyte caused by sintering shrinkages.

Cathode deposition will be accomplished using plasma spraying to deposit a 0.015-0.020" thick layer of porous $\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$. Developing a method to spray the cathode material onto the interconnect without filling the channels will be the primary challenge for this layer. Achieving the desired level of porosity and adhesion appears to be fairly straightforward.

Deposition of dense, defect-free electrolyte layers having a thickness of 0.001-0.002" will be the difficult step in cell fabrication. The B&W team is currently developing a modified plasma spray system in which fine yttria stabilized zirconia (YSZ) powders (<30 μm diameter) are sprayed onto the porous cathode layer. Although low pressure plasma spray techniques have been successfully employed by other researchers to form dense YSZ films [13-15], we plan to focus only on atmospheric spraying, as this approach is more amenable to manufacturing [12,16,17].

Anode deposition will likewise be performed by plasma spraying Ni, NiO and YSZ powders. To achieve adequate electrical conductivity but minimize the thermal expansion coefficient, Ni contents in the range of 30-45% will be employed. Although adhesion to the YSZ electrode should not be a problem, achieving the proper level of porosity and minimizing damage to the electrode layer will require some effort. It should be noted that numerous researchers have successfully employed plasma spraying to fabricate anode [1,12] and cathode [1,18] layers. Thus, we are not doing anything particularly novel for these layers.

Stack formation will be accomplished by stacking individual cells on top of each other, as illustrated in Figure 2, and then heating the stack to about 1200° to 1400°C to bond the cells together. This step is considered the most important one in the sequence, as the quality of the bond will dictate the overall performance of the stack. The B&W Team is presently investigating techniques based on diffusion bonding and brazing using Ni-based alloys to achieve a high-quality joint.

RESULTS TO DATE - PHASE I

The objective of the Phase I effort is to demonstrate a 2" square, 3-5 cell stack that operates at greater than 0.6 V/cell and 500 mA/cm² (of cell area). Although the program was only initiated in April 1992, we have made good progress in several areas, as discussed in the following paragraphs.
Interconnect Fabrication

Babcock & Wilcox has successfully developed a dry pressing and sintering process to fabricate thin, flat chromite interconnect plates. The efforts required to complete this work included evaluation of: (1) powder compositions and sources; (2) powder preparation and pressing parameters; (3) binder burnout, sintering, and creep flattening parameters; and (4) machining of sintered plates to form the channels.

Initial work was conducted using $\text{La}_x \text{Sr}_{1-x} \text{CrO}_3$ powders from two suppliers having varied cation ratios. These powders were found to be very difficult to sinter. Attempts to hot press these powders were also largely unsuccessful, as reaction of the powders with the graphite dies could not be readily avoided. Subsequent work was performed using powders having the general formula $\text{La}_x \text{Ca}_{1-x} \text{Cr}_x \text{Co}_{1-y} \text{O}_3$ (LCCC); these powders were readily sintered in air to greater than 95% of theoretical density. These sintered materials yielded electrical properties equal or superior to those measured by other investigators for similar compositions [4,5]. Electrical conductivities, measured in air as a function of temperature, for two of the B&W chromite materials are shown in Figure 3.

Dry pressing of $3'' \times 3''$ green plates was accomplished with a double-action 50-ton hydraulic press at pressures of 4000 to 8000 psi. To prepare the powders for pressing, a ball milling process was used to break up powder agglomerates, mix in the binder, and granulate the powder/binder mix. The binder phase used consisted of a mixture of polyvinyl alcohol and polyethylene glycol. A heating schedule for binder burnout and sintering of the LCCC plates was developed with the aid of TGA and dilatometry experiments. A typical shrinkage curve for the double-doped chromite material is shown in Figure 4. The ability to sinter this material to high densities in air is derived from a transient liquid phase which appears at about 900°C. This temperature corresponds to the onset of rapid densification in the shrinkage curve. Densities greater than 95% of theoretical are now routinely achieved by sintering at 1400-1500°C.

Cathode Fabrication

At the time of this writing, only preliminary plasma spray trials on alumina substrates had been completed for deposition of the porous $\text{La}_x \text{Sr}_{1-x} \text{MnO}_3$ (LSM) cathode. A commercially available LSM powder having an average particle size of 100 μm was sprayed using current and voltage settings in the range of 300-400 amps and 75-85 volts, respectively. Initial results have been very encouraging, as an adherent coating having about 40% porosity was obtained. Future work will entail developing the appropriate spraying parameters for the LCCC substrate, verifying the
adhesion and electrical properties, and establishing a method to spray onto the channeled interconnect while not filling the channels.

Electrolyte Fabrication

Although only initial spraying trials have been conducted for the YSZ electrolyte, it appears that atmospheric pressure spraying of fine powders will yield a sufficiently dense, gas tight layer. Initial trials were conducted using current and voltage settings of 400-500 amps and 60-80 volts, respectively. The YSZ was sprayed onto porous alumina substrates that were heated to about 600 to 800°C. As shown in Figure 5, a typical YSZ deposit from 20-30 μm powders appears to have a density greater than 90% of theoretical; however, significant microcracking of the film was observed. Such microcracking will lead to poor performance of a fuel cell and must be eliminated. Although the cause of the microcracking has not been verified, it is suspected that the thermal expansion mismatch between the alumina substrate and the YSZ contributed to this problem. Future efforts will be directed at improving the densities of the YSZ films and eliminating the microcracking. The use of porous YSZ and LSM substrates and additional modifications to the spray gun will be the focus of these investigations.

SUMMARY

In early 1992, B&W initiated a multiphase program to develop and commercialize an advanced planar SOFC. A primary goal in our efforts will be to establish a low-cost manufacturing capability for reliable, high-quality SOFC power modules. Based on an extensive study of current and developing SOFC technologies performed in 1991, we believe that a cross-flow bi-polar stack configuration in which the individual cells are fabricated through sequential deposition of the active layers has the most attractive combination of manufacturability and operating performance. To insure the maximum probability of success for the B&W program, a multidisciplinary team having extensive experience in ceramic fabrication and SOFC technologies is being formed.

Initial results of our Phase I (Concept Feasibility Demonstration) efforts have been very positive. Materials and processes have been identified which allow fabrication of dense interconnect plates - using dry pressing and air sintering. Plasma spray procedures have been developed which allow deposition of adherent, porous cathode layers and thin, dense electrolyte layers. Future efforts will be directed at optimizing the deposition processes for each of the requisite layers and developing methods to bond individual cells into stacks. Evaluation of interfacial properties using AC impedance techniques and characterization of electrochemical performance for single cells and small stacks will also be performed.
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Figure 1
Advanced Planar SOFC Concept:
3 Cell Stack
Figure 2
Stacking of Individual Cells
Figure 3
Electrical Conductivity vs. Temperature
For LCCC Interconnect Material

Figure 4
Typical Shrinkage Curve for LCCC
Figure 5
SEM Photomicrograph of Plasma Sprayed YSZ Electrolyte