PLANAR SOFC STACK WITH LOW-COST MULTI-LAYER CERAMIC INTERCONNECT

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ABSTRACT

The SOFCo-EFS stack utilizes a multi-layer ceramic (MLC) interconnect that is designed to have a close thermal expansion match with zirconia-based cells. The MLC interconnect is fabricated using multiple layers of YSZ tape, with each layer containing conductive vias to provide for electrical current flow through the interconnect. Fuel and air supply to cells are accomplished through the use of flow passages in the layers. This paper provides an update on the development status for the MLC interconnects and stacks, with emphasis on low-cost conductor materials for the vias. Separate low-cost materials have been developed for the air-side and fuel-side vias, and successfully implemented into 10 cm interconnects. Planar stacks have been assembled using electrolyte-supported cells and tested. Special instrumentation was used for these stacks in order to separate area specific resistance (ASR) contribution from each component.

INTRODUCTION

SOFCo-EFS Holdings LLC is developing a planar solid oxide fuel cell (SOFC) that utilizes a unique multi-layer ceramic interconnect. The patented SOFCo-EFS approach combines advanced SOFC materials with the manufacturing technology and infrastructure established for multi-layer ceramic (MLC) packages for the microelectronics industry. With the proper selection of SOFC materials, implementation of MLC fabrication methods is expected to lead to SOFC stacks that will provide superior performance and reliability at reduced costs (e.g., $150 per kW) relative to competing SOFC designs. In order to achieve the stack cost targets, low-cost raw materials must be used in the manufacture of the MLC interconnect.

In planar SOFC stacks, the role of the interconnect is twofold; it acts as physical barrier to separate fuel gas and air, preventing cathode materials from being exposed to the reducing environment of the fuel and preventing the anode materials from contacting with oxidizing atmosphere. It also provides electrical connection between cells in the stack. Since SOFC stacks operate at high temperatures, generally in the range of 700 to 1000°C, interconnect materials have to meet the following requirements: 1) Interconnect must be stable in terms of dimensions, microstructure, chemistry, and phase at operating temperature in both reducing and oxidizing atmospheres; 2) Interconnect must be chemically compatible with electrode materials, that is, there should be no reaction or contamination to anode or cathode during operation; 3) Interconnect should have...
matched coefficient of thermal expansion (CTE) with the cell to minimize thermal stress during operation and thermal cycling; 4) Interconnect should have adequate electrical conductivity at fuel cell operating conditions, with essentially no oxygen ion conduction; 5) Interconnect material should possess sufficient strength and toughness to maintain mechanical integrity of the fuel cell stack; and 6) Interconnect has to be gas-tight for both oxygen and hydrogen at operating conditions to minimize the inter-diffusion of hydrogen and oxygen. These requirements place significant constraints on the selection of suitable materials for SOFC interconnects.

Lanthanum chromite (LaCrO₃) is the most common ceramic interconnect material used for SOFC stacks (1). Undoped lanthanum chromite has an electrical conductivity of 1 S/cm at 1000°C and an average thermal expansion coefficient of 9.5x10⁻⁶/°C. A number of authors (2-10) have addressed the nature of the defect chemistry and electrical conductivity of doped LaCrO₃. Doping with Mg, Sr, Ca, Ni, etc., increases the electrical conductivity of lanthanum chromite to the range of 2 to 18 S/cm at 700°C. The thermal expansion coefficient is in the range of 10 to 13x10⁻⁶/°C. The investigations show that doped LaCrO₃ has sufficient electrical conductivity to perform as an interconnect, as long as the operating temperature is above 800°C. Below 800°C, the electrical conductivity of doped LaCrO₃ is reported to experience substantial degradation (11). The issues for LaCrO₃ interconnect are: 1) poor sinterability due to chromium evaporation; and 2) strength degradation and dimension change with decreasing oxygen partial pressure, especially when pO₂ is below 10⁻⁸ atm.

Metallic interconnects, such as chromium-based alloys and iron-based alloys, are another choice for SOFC stacks with intermediate and lower operating temperatures (800°C or lower) (1). The advantages of metallic interconnects are: 1) lower cost for both the raw materials and interconnect fabrication, and 2) mechanical integrity. Since the CTE of metallic interconnect can be easily adjusted to 13 – 15x10⁻⁶/°C, they are especially suitable for SOFC stacks using anode-supported cells. The reason is anode-supported cells use a NiO-YSZ substrate as the primary structural element. As a result, the cells have a CTE of 12.5 to 13.5x10⁻⁶/°C, depending on the ratio of NiO to YSZ. The issues for metallic interconnects are: 1) oxide scale formation and/or delamination on the surface at high temperatures in air, which will reduce interconnect conductivity; and 2) chromium evaporation and deposition at the interface between cathode and the electrolyte (12) at operation temperature, which poisons the cathode and reduces cell performance.

SOFCo-EFS is developing a novel planar SOFC stack that has the potential to provide superior performance and reliability at reduced costs relative to competing SOFC designs. The SOFCo-EFS stack utilizes a multi-layer ceramic (MLC) interconnect that is designed to have a close thermal expansion match with zirconia-based cells. The MLC interconnect is fabricated using multiple layers of yttrium stabilized zirconia (YSZ) tape, with each layer containing conductive vias to provide for electrical current flow through the interconnect. Fuel and air supply to cells are accomplished through the use of flow passages in the layers. Over the past five years, SOFCo-EFS has made significant progress in the development of the MLC interconnect. Stacks using 10 cm interconnects have been routinely operated, and initial efforts to scale up to larger sizes have shown good progress. However, these interconnects have used expensive conductor materials for the vias. Development and implementation of low-cost via materials will be required to achieve cost-competitive stack technology.
This paper provides an update on the development status for the MLC interconnect, highlighting SOFCo-EFS’ development of low-cost conductor materials for the vias. Separate materials have been developed for the air-side and fuel-side vias, and successfully implemented into 10 cm interconnects. Planar stacks have been assembled using electrolyte-supported cells and tested. Special instrumentation was used for these stacks in order to separate area specific resistance (ASR) contribution from each component, such as the cells, fuel side vias, air side vias, etc. Factors causing ASR degradation of low-cost via materials are discussed. Performance and post-analysis results for the stacks are presented.

**LOW-COST VIA MATERIALS DEVELOPMENT**

Development of low-cost via materials has been a challenge because of the numerous requirements that must be met. First, the vias are formed by screen printing thick-film pastes into holes within the YSZ tape layers, followed by lamination and co-firing. As a result, the sintering behavior and thermal expansion must be matched with YSZ. Second, the via materials must not react with YSZ during co-firing and achieve a high conductivity. Third, the via materials must be compatible with the SOFC operating conditions, maintaining high electrical conductivity under the reducing (fuel-side) or oxidizing (air-side) environment at high temperature for extended periods of time.

To meet all these requirements, SOFCo-EFS has developed two kinds of materials for use as conductive vias in the fuel- and air-side of the multi-layer ceramic interconnect. The fuel-side via material is a nickel cermet using NiO as a starting material and fired in air. During stack operation the NiO can be reduced in-situ to form Ni metal as the electrically conductive phase. The air-side via material is a conductive perovskite ceramic. Both fuel- and air-side via materials have good match with the YSZ multi-layer ceramic in sintering behavior, all of which can be densified at the same temperature range in air.

The properties of the low-cost via materials are summarized in Table 1. The ceramic interconnects are made from 3mol% Y2O3-doped zirconia which has a CTE of 10.8x10^-6/°C from room temperature to 950°C. The air-side via material has a CTE of

| Table 1. Low-Cost Via Material Properties. |
|-------------------------------------------|
| CTE, x10^5 °/C | Conductivity at 850°C, Siemens/cm |
|----------------|----------------------------------|
| Air-side via   | 11.0                             |
|                | >500                             |
| Fuel-side via  | As-fired state 11.4 (RT-1100°C)  |
|                | Non-conductive                   |
|                | Reduced state 11.4 (RT-950°C)    |
|                | >3000                            |
| YSZ interconnect | 10.8 (RT-950°C)                |
11.0 x 10^{-6}^\circ \text{C}, which is very good match with YSZ interconnect. The CTE for fuel-side via material is 11.4 x 10^{-6}^\circ \text{C} for both the as-sintered and reduced states. The electrical conductivity of the fuel-side via material (3000 S/cm) is much higher than that for air-side material (500 S/cm) at 850^\circ \text{C}.

Material conductivity data and via dimensions, such as via diameter and length, were used to calculate expected area specific resistance (ASR) contributions for the vias. The ASR contribution was estimated to be about 0.03 ohm-cm^2 for the air-side vias per interconnect and 0.008 ohm-cm^2 for the fuel-side vias per interconnect. Multi-layer ceramic interconnects fabricated using the low-cost via materials and electrolyte-supported cells were used to assemble the planar SOFC stacks for evaluation of via performance. State-of-the-art electrolyte-supported cells have ASR values in the range of 0.5 to 1.3 ohm-cm^2. For this study, commercial electrolyte-supported cell having an ASR of 1.2 ohm-cm^2 were used. With these cells, the stack ASR was projected to be about 1.25 ohm-cm^2 (based on an interconnect ASR contribution of 0.05 ohm-cm^2 or less). Based on these estimates, the low-cost via materials developed by SOFCo-EFS should have a low ASR contribution, and therefore meet the fuel cell stack performance requirements.

MULTI-LAYER CERAMIC INTERCONNECT FABRICATION

SOFCo-EFS multi-layer ceramic interconnects were fabricated using standard MLC manufacturing processes and thick film technology. First, YSZ ceramic green tape was tape cast from ceramic slip composed of YSZ powder, binder, plasticizer, dispersant, and solvent. The tape cast slip was dried under controlled temperature profile and air flow. Second, single layers of YSZ green tape were punched to form fuel or air flow channels, and via holes. Third, the via holes were filled with the appropriate thick film inks by screen printing. Fourth, single layers of YSZ green tape were laminated together, by thermo-compression or adhesive lamination. Fifth, after excising to the desired dimension, the green laminate was fired at high temperature (>1300^\circ \text{C}), where the YSZ body and via materials were densified to achieve >95% of theoretical density.

Figure 1 illustrates the key steps in the fabrication of multi-layer ceramic interconnects and the conductive vias through all YSZ layers. The center layer is solid to separate fuel gas and air, which is called separator layer. The current via material is a precious metal cermet, which is thermally stable and highly conductive in both reducing and oxidizing atmospheres at operating temperature. However, due to the high cost, the precious metal has to be removed from the SOFC stack for commercialization. Since the low-cost fuel-side via material is stable and has high conductivity only in a reducing atmosphere and the low-cost air-side via material is stable and has high conductivity only in an oxidizing environment, a precious metal cermet is still used in the separator layer to separate fuel gas and air. After implementation of low-cost via materials into the MLC interconnects, the new via structure is shown in Figure 2.
Figure 1. Multi-layer ceramic interconnect structure and key steps in the fabrication: (a) YSZ tape blanks with punched flow channels and via holes; (b) green interconnect, after lamination and excising; (c) fired interconnect; and (d) a cross-section of vias within the YSZ layers.

Figure 2. Conductive via structure with low-cost via materials.

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Stack Instrumentation and Testing Results

Multi-layer ceramic interconnects were successfully developed and fabricated at SOFCo-EFS. After sintering, the multi-layer ceramic interconnects were inspected for via
continuity (percentage of conductive vias), cracks, delamination, warpage, etc. Only those interconnects meeting specification were used in stack testing. To evaluate the low-cost via materials, commercial 3YSZ electrolyte-supported cells (ASR of about 1.2 ohm-cm²) were used to assemble instrumented short stacks. SOFCo-EFS unique all ceramic planar SOFC stack design and stack building procedures are described elsewhere (13). For this study, full instrumentation was used to obtain the ASR contribution from each component, as illustrated in Figure 3. The lay-out of the first stack, from bottom to top, was metallic current collector, standard ceramic full interconnect with the precious metal via material, cell, half-fuel interconnect (HF, fuel-side layers plus separator layer) with low-cost via material (LVM), half-air interconnect (HA, air-side layers plus separator layer) with LVM, cell, full interconnect with LVM, cell, standard interconnect with precious metal via material, and metallic current collector. Between each component, a thick film ink was used to form an electrically conductive path. From the instrumentation shown in Figure 3, the ASR contribution from following components were obtained: three electrolyte-supported cells, half-fuel interconnect with LVM, half-air interconnect with LVM, full interconnect with LVM, and the top standard interconnect (IC) with precious metal cermet vias.

![Diagram of stack components and instrumentation](image)

**Figure 3. Three cell short stack with low-cost multi-player ceramic interconnect and instrumentation for ASR breakdown.**

The electrochemical performance of the three-cell short stack is shown in Figure 4. For this short stack, conservative testing conditions were used (i.e., low current density and low fuel utilization). The stack was tested at a constant voltage of 0.8 V/cell. The stack performance stabilized after about 100 hours, at which time the current density was ~82 mA/cm² and the fuel utilization was ~15%. The fuel was humidified wet 50%H₂:50%N₂. The three electrolyte-supported cells had a fairly consistent performance, with an average ASR of 1.74 ohm-cm², which was higher than expected. The standard interconnect with precious metal cermet vias had a stable and low ASR of 0.06 ohm-cm². The half-air interconnect with low-cost via material also showed a stable and low ASR of 0.07 ohm-cm², which is comparable to that of the standard interconnect. Before building the stack, the half-fuel interconnect was pre-reduced, thus Ni metal existed in fuel-side vias. The
ASR contribution was relatively low, 0.23 ohm-cm², when the testing was started, and then increased with time and stabilized at an ASR of 0.96 ohm-cm² (after 40 hours testing). The full interconnect with LVM was reduced in-situ during stack testing, because the air-side via material is unstable at low pO₂ environment. The ASR of the full interconnect was high when testing started, up to 7 ohm-cm², and then decreased with time and leveled to an ASR of 1.8 ohm-cm² after 180 hours testing. It is believed that the drop in ASR was due to the reduction of NiO to Ni metal in the fuel-side vias. These data indicated that the ASR of fuel-side via material was not as low as expected. After 118 hours testing, the fuel composition was changed to humidified 75%H₂:25%N₂. This change resulted in significant reduction of cell ASR from 1.74 to 1.0 ohm-cm², and an increase of stack current density from 80 to 115 mA/cm².

Figure 4. ASR contribution from each component of the three-cell short stack during short-term testing (Testing temperature: 850°C, fuel: H₂-N₂ mixture with 3% H₂O, low fuel utilization).

Post-Test Analysis of Short Stack

The short stack was disassembled for inspection after testing. All cells and interconnects were in good shape, and no cracks and other physical defects were created. Both half-fuel interconnects and the full interconnect with low-cost via materials were cross-sectioned and examined. Special attention was paid to the via interface between the separator and fuel-side layers.

There are two possible reasons for the high ASR of fuel-side via material: 1) oxidation of the Ni to form NiO, or 2) deleterious materials interactions. Since the fuel-side via is a nickel cermet, it exists as Ni metal in low pO₂ and NiO in high pO₂ environments. Based on interconnect design, the separator layer is a precious metal cermet which is a good conductor in both low and high pO₂ environments. These vias are also gas-tight, and can effectively separate fuel and air. However, if oxygen has higher permeability in separator layer via material than hydrogen, oxygen may diffuse through separator via material to fuel-side via material and create a high local pO₂ environment at the interface, which could oxidize Ni to NiO and lose conductivity. Oxygen and hydrogen permeability
measurements for the separator layer via material showed that oxygen permeability is about twice that for hydrogen. This would suggest that there is possibility that Ni metal at the interface of separator and fuel-layer via was oxidized into NiO. However, since the fuel-side via material is porous after reduction, there should be enough hydrogen at the interface to react with the oxygen if it diffuses through separator layer via. To determine whether NiO exists at the interface, the fuel-side via material near the separator layer interface was examined by XPS (Perkin-Elmer PHI-5600). It was confirmed that nickel exists as Ni metal instead of the oxide. Based on preliminary analysis and examination, a locally high pO2 at the interface of separator and fuel-layer via was determined not to be an issue.

To determine if other interface reactions had occurred, more detailed SEM analyses were performed. Figure 5 shows the separator and fuel-layer via interface for the half-fuel interconnect. The top half of the picture shows the via material in separator layer; the white phase is the precious metal. The bottom of the picture shows the via material in fuel-side layer, where the lighter phase is Ni metal. Near the interface, a Ni depletion zone is observed (rich in YSZ), which is about 30μm wide. This Ni depletion zone explains why the ASR of half-fuel interconnect increased with time and eventually stabilized. When testing started, it appears that Ni diffused from the fuel-side vias into the separator layer vias due to the concentration driving force. With diffusion, Ni metal accumulated in separator layer via material, thereby reducing the driving force and eventually establishing equilibrium.

The microstructure of the interface between the separator layer and fuel-side layer via materials in the full interconnect is shown in Figure 6. In this picture, the top shows the fuel-side via material near the interface, while the bottom shows the separator layer via material near interface. Clearly, the interface microstructure of full interconnect is worse than half interconnect. With Ni migration away from the fuel-side via at the interface, a porous layer (~4μm thick) was formed. The material left in the porous layer is a mixture of multiple components rich in non-conductive ceramic phase. This observation could explain why the full interconnect had a higher ASR than the half-fuel interconnect. Ni

![Figure 5. SEM image of the interface of the precious metal cermet (top) and Ni cermet via (bottom) materials for the half-fuel interconnect after stack testing.](image-url)
metal migration from fuel-side via material into separator layer via material resulted in a low conductivity porous layer at via interface. This appears to be the major cause of the unexpected high ASR of full and half interconnects incorporating the low-cost fuel-side via materials.

Figure 6. SEM image of the interface of the precious metal cermet (bottom) and Ni cermet via (top) materials of full interconnect after stack testing.

Via Materials Modification

In order to solve the interface issue, the via materials were modified to provide more conductive phase in the vias and to reduce driving force for Ni migration at the via interface. To effectively evaluate the new via materials, test specimens were designed to simulate the interconnect structure. YSZ tape blanks were punched with standard via holes. The via holes of one layer were filled with the improved separator layer via material and another layer was filled with improved fuel-side layer via material. After via filling, the two tape blanks were laminated together to form a bi-layer structure. The laminate was co-fired using same process conditions used for standard ceramic interconnects. After sintering, the bi-layer specimen was reduced in forming gas at 850°C. Continuity and via resistance were measured by two probes at room temperature. After measurement, the bi-layer was heated to 850°C under 4%H2—96%N2 forming gas for a via materials degradation study. Electrical properties of via materials before and after modification are listed in Table 2. It appears that electrical properties of via materials have been significantly improved by modifying the composition.

Using the new via materials, multi-layer ceramic interconnects were fabricated again in SOFCo-EFS' prototyping lab. After pre-reduction of a half-fuel interconnect by heating to 850°C under 4%H2 forming gas, via resistance was measured by the four-point method. Figure 7 shows the four-point resistance test results for the new via materials at 850°C under 4%H2 forming gas. During the 200 hour test period via resistance is stable and under 0.2 ohms, which is equivalent to an ASR of 0.04 ohm-cm² per half-fuel interconnect.

Using the new multi-layer ceramic interconnects with improved via materials, an instrumented two-cell short stack was built. A higher current density, 150 mA/cm², was
Table 2. Electrical Properties of Bi-layer Specimens.

|                                | Old via material | Modified via material |
|--------------------------------|------------------|-----------------------|
| Continuity, %                  | 69               | 99                    |
| Average resistance, ohm/via    | 8                | 0.10                  |
| Resistance after 160 hrs aging at 850°C under 4%H₂ forming gas, ohm | N/A              | 0.24                  |
| Continuity after 160 hrs aging at 850°C under 4%H₂ forming gas, % | N/A              | 99.5                  |

Figure 7. High temperature resistance of new fuel side via material in 4%H₂-96%N₂ forming gas.

Figure 8. ASR contribution from each component of two-cell short stack (Testing temperature: 850°C, H₂-N₂ mixture with 3% H₂O, current density: 150 mA/cm²).

used for this second short stack. After 200 hours of operation, the ASR contribution for the two half-fuel interconnects was at 0.09 ohm·cm² and appeared to be relatively stable (Figure 8). One of the half-air interconnects showed unacceptable degradation (increasing
ASR contribution. The source of the degradation is unknown at present. Post-analysis will be performed after the stack is shut down.

SUMMARY

Low-cost conductive materials have been developed by SOFCo-EFS to replace the precious metal cermet via materials used in the fabrication of multi-layer ceramic interconnects. Short SOFC stacks were built using electrolyte-supported cells and low-cost multi-layer ceramic interconnects. These stacks were tested using special instrumentation, allowing the ASR contribution from each component to be separated. Testing results to date indicate that multi-layer ceramic interconnects using the low-cost via materials have a low ASR contribution. However, further work is required to demonstrate the required repeatability and long-term stability of these interconnects.

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