DEVELOPMENT OF LOW-COST ALLOY SUPPORTED SOFCs

Steven J. Visco, Craig P. Jacobson, Igor Villareal*, Andy Leming
Yuriy Matus and Lutgard C. De Jonghe
Lawrence Berkeley National Laboratory
Materials Sciences Division
1 Cyclotron Road, Berkeley, CA 94720, USA

* Ikerlan Applied Research Center
Minano, Spain

ABSTRACT

The LBNL group has been developing ferritic steel supported solid oxide fuel cells. The use of ferritic steel as a support for electrode supported solid oxide fuel cells greatly reduces the raw materials cost and improves the strength of the thin-film cells. The basic design includes the use of a high-strength FeCr support, a thin interlayer electrode (Ni-YSZ or other), and a thin electrolyte film. The entire structure is fabricated through co-firing of the three layers in a reducing environment. This paper describes the preliminary performance of the metal supported cells, as well as a variety of possible interlayer electrodes.

INTRODUCTION

Development of solid oxide fuel cells dates back to work in late 1950's at the Central Technical Institute in The Hague, Netherlands, at Consolidation Coal Company in Pennsylvania, and General Electric in Schenectady, New York. In the early 1960's, researchers at Westinghouse started work on calcia stabilized zirconia, leading ultimately to the development of the tubular solid oxide fuel cell technology. Over the past several decades a number of commercial developers, national laboratories, and university researchers have made significant advances in solid oxide fuel cell development due to improvements in electrode kinetics, interface stability, electrolyte conductivity, and cell and stack design. In particular long-term testing of solid oxide fuel cell systems by Siemens Westinghouse Power Corporation have demonstrated that SOFC generators produce power at high efficiencies, and with minimal degradation of performance over 10's of thousands of hours (1). Funding for the development of SOFC systems appears to be increasing in the U. S. and Europe, both for public and privately funded efforts. Still, even though the demand for power generation technology is high, SOFC systems have not yet made significant penetration into the energy marketplace. The lack of commercial SOFC systems is almost entirely due to the high price of the technology at the current stage of development. Accordingly, many developers have focused on cost reduction as the key strategy for successful commercialization of SOFC technology. The U. S. Department of Energy has launched the Solid State Energy Conversion Alliance (managed by the National Energy Technology Laboratory) in order to deliver cost-competitive SOFC generators to the marketplace; the targeted system cost is $400 /kW.
The complete system consists of fuel cell stack, power electronics (DC-AC inverter), and balance-of-plant. Assuming that each of the sub-systems account for 1/3 of the total cost, the stack cost should be about $130/kW. Since development of the stack represents the highest technical risk, it is also where costs often spiral out of control. Many developers have utilized high-cost materials and/or processes to solve the technical issues related to performance, seals, and stack longevity. Unfortunately, once a stack design is mature, it is often difficult to remove cost simply through engineering.

A number of companies are now pursuing solid oxide fuel cells for operation at reduced temperatures (650 to 800°C) as a potential strategy for cost reduction; at these temperatures the choice of materials to build the stack is broader than for cells operating at 900 to 1000°C. Typically, this is accomplished by moving to electrode supported fuel cell design where a thin electrolyte layer (10 to 20 μm) is supported on a porous Ni cermet anode or porous cathode. Using this geometry, several groups worldwide have reported excellent power densities at reduced temperatures (2, 3). Most groups developing electrode supported thin-film electrolyte SOFCs are also replacing expensive ceramic lanthanum chromite-based interconnects with inexpensive ferritic steel interconnects. Although this approach has large potential cost savings, issues of high temperature corrosion of steel under reducing and oxidizing conditions, and interfacial stability at the electrode/interconnect boundary are of critical importance to the success of these efforts.

**APPROACH**

The use of anode supported thin-film cell design offers substantial reduction in the ohmic losses across the electrolyte. However, by moving to thin electrolytes, the structural support for the SOFC becomes the porous electrode. For anode supported designs, the support becomes the Ni-YSZ cermet, consequently it is unlikely that anodes thinner than 1 mm will have sufficient strength for assembly into robust stacks. This design constraint also has an impact on cell cost since both Ni and YSZ are expensive as raw materials.

In Table 1 an estimate of raw materials cost is shown for an anode supported cell where a 2 mm anode consisting of a 50/50 mix of Ni/YSZ having 30% porosity supports a thin YSZ electrolyte and a 0.5 mm steel interconnect plate. At an operating power density of 300 mW/cm² the cost of raw materials alone for this cell is over $110 /kW. This does not include processing costs, or stack assembly costs. Conversely, in Table 2 the same estimate is shown for a steel supported cell having a 0.5 mm, 30% porous support and a 0.5 mm steel interconnect plate with a 20 μm Ni-YSZ electrode layer and a 20 μm YSZ film. The raw materials cost for the steel supported cell is a factor of 7 times lower, and well within the SECA target range.

Alternatives to anode-supported geometries include cathode supported designs and anode supported designs where the support is comprised mainly of inexpensive materials with desirable mechanical and electrical properties and incorporate a thin electrocatalytic layer adjacent to the electrolyte. Since most of the electrode reaction occurs over a distance of several microns, the majority of the Ni-YSZ does not participate in the electrode reaction but merely serves as a current collector and mechanical support. The high cost of Ni and
YSZ provides strong motivation to replace electrochemically inactive bulk of the anode support by a low-cost alternative.

Table 1. Cost of Raw Materials for 2 mm anode Supported SOFC at 300 mW/cm².

| Component      | Thickness | Density | Cost/kg | SOFC Cost/$kW |
|----------------|-----------|---------|---------|---------------|
| YSZ powder     | 700       | 6       | 60      | $84           |
| Steel Powder   | 500.0     | 7.8     | 5       | $7            |
| LSM            | 50        | 6       | 10      | $1            |
| Ni             | 700       | 8.9     | 10      | $21           |
|                |           |         |         | Total $112/kW |

Table 2. Cost of raw materials for 0.5 mm steel supported SOFC at 300 mW/cm²

| Component      | Thickness | Density | Cost/kg | SOFC Cost/$kW |
|----------------|-----------|---------|---------|---------------|
| YSZ powder     | 30        | 6       | 60      | 3.6           |
| Steel Powder   | 850       | 7.8     | 5       | 11.1          |
| LSM            | 50        | 6       | 10      | 1.0           |
| Ni             | 10        | 8.9     | 10      | 0.3           |
|                |           |         |         | Total $15.9/kW |

Figure 1. Electrolyte supported and electrode supported SOFC designs.

The use of ferritic steel supports for the solid oxide fuel cell element has the potential of greatly lowering the raw materials cost for the stack. Stainless steel is used in exceptionally large volumes commercially, and is almost an order of magnitude less expensive than yttria stabilized zirconia. Additionally, alloys such as ferritic steel have very high electronic conductivity, good corrosion resistance, and thermal expansion coefficients that are well matched to YSZ. The use of an alloy support also simplifies stack design in that the alloy support can be welded or brazed. The fabrication of thin electrolyte films onto porous steel supports can be accomplished by a number of techniques. One approach involves the use of plasma-spray techniques to deposit dense YSZ films onto invariant porous metal supports (4). This approach has the advantage of using previously sintered porous metal structures as substrates for plasma spray deposited
films, and solid oxide fuels cells fabricated in this manner have demonstrated impressive levels of performance. However, ceramic powders for plasma-spray are expensive, and the technique itself is costly in terms of the cost/hour and rate of material deposition.

An alternative approach is to use conventional ceramic and metal powder processing technology to co-fire the appropriate metal supported microstructure. In order to co-fire a metal supported SOFC, it is necessary sinter such structures in a reducing environment. Since the ferritic steels used by our group are chromia formers (18 to 26% Cr), the pO2 must be very low to avoid the formation of Cr2O3 during sintering; this would impede densification of the metal support. Accordingly, the metal/ceramic structures are fired under a 4% hydrogen/inert gas mixture as shown in Figure 1; titanium sponge is used to scavenge any moisture that might be present in the gas feed.

![Figure 2. Sintering of metal supported FeCr/Ni-YSZ/YSZ fuel cells in reducing environment.](image)

In the fabrication of NiO-YSZ supported thin-film cells, pore formers such as corn starch and graphite are commonly used to maintain porosity of the sintered NiO-YSZ/YSZ structures. Pore formers give rise to macro-porosity in the anode support for gas transport. During the initial reduction of the NiO-YSZ anode to form Ni-YSZ, additional porosity is introduced into the structure. Of course, this is not the case for NiO-YSZ sintered in a reducing environment since the NiO is rapidly converted to Ni during sintering. Consequently, it is critical to maintain porosity in the electrocatalytic Ni-YSZ layer during sintering. Also, burnout of binders during sintering in hydrogen is problematic since pyrolysis will lead to the formation of carbon and the subsequent formation of low-melting carbon steel. This is avoided by burnout of the organic binders in both the FeCr support and NiO-YSZ layer in air at a temperature of about 400°C; some oxidation of the FeCr structure will occur, but this is removed during high temperature sintering in a reducing atmosphere. Sintering profiles of green YSZ disks measured at LBNL in air and in 4% hydrogen showed no measurable effect of the pO2 on the sintering rate of YSZ; consequently the densification of YSZ thin films should not be affected by the conditions needed for co-firing metal supported structures.

There are also several alternatives to the use of a Ni-YSZ interlayer between the FeCr support and YSZ thin-film electrolyte. Clearly, the interlayer must exhibit low overpotential for hydrogen oxidation, and stability against the FeCr support and YSZ electrolyte as well as stability in reducing conditions at high temperatures. Recently,
PNNL presented impressive results for a new class of doped strontium titanate anodes (5) that exhibit comparable performance to nickel based anodes. Such materials might play a role in metal supported SOFCs. The figure below indicates a range of potential materials for the electrode interlayer in a metal supported cell.

![Diagram showing potential materials for electrode interlayer in a metal supported SOFC.]

**Figure 3. Alternative anode interlayer for metal supported SOFCs.**

**EXPERIMENTAL**

**Thin Film Metal Supported Structures**

Yttria stabilized zirconia, 8YSZ, was obtained from Tosoh (Japan). A variety of 446 stainless steel powders with chromium content in the range of 18 to 30% were obtained from commercial suppliers including Praxair Specialty Ceramics (USA) and Ametek (30% Cr); this level of Cr content is sufficient to prevent substantial oxidation of the alloy in the SOFC environment. The powders are classified using steel mesh sieves in order to have a particle size distribution in the range of 35 to 75 μm in diameter. The resulting FeCr powders are mixed with 5 wt% steric acid dissolved in isopropyl alcohol, and dried. The resulting mixture is pressed in a 1 inch diameter steel at die at 15,000 lbs. pressure to a green density of about 60% of theoretical. The steel/steric acid compacts are pre-fired at 400°C to remove the steric acid binder. A mixture of NiO and YSZ (50/50 wt%) is combined with 5 wt% polyvinylbutyral (PVB) and 5 wt% polyethylene glycol (PEG) of molecular weight 6000 dissolved in isopropyl alcohol and mixed in an attrition mill for 1 hour; the resulting slurry is applied by doctor blade or screen printed onto the stainless steel support; the binder is removed at 600°C in air for 1 hour. Alternatively, an interlayer comprised of 45 wt% strontium titanate, 5 wt% NiO, and 50 wt% YSZ was used instead of NiO-YSZ; the slurry mixture was prepared and deposited on the FeCr support in the same manner as for NiO-YSZ interlayer. Then, a thin electrolyte layer of...
YSZ is deposited onto the FeCr/NiO-YSZ (or FeCr/SrTiO3-NiO-YSZ) structure by dip-coating or aerosol spraying of a dispersion of YSZ in isopropyl alcohol. Finally, the FeCr/NiO-YSZ/YSZ is placed in a controlled atmosphere furnace (Figure 2) and sintered between 1250°C and 1350°C in 4% H2. After firing, an air electrode is aerosol sprayed or screen printed onto the FeCr/Ni-YSZ/YSZ structure; typically either Pt paste or La0.6Sr0.4Co0.2Fe0.8O3/Pt fired onto the YSZ electrolyte at 900°C in air.

**Thick Film YSZ Structures**

In order to determine the suitability of a variety of potential interlayer electrodes for application in FeCr supported cells, electrolyte supported cells having reference electrodes were employed. Yttria stabilized zirconia plates of between 0.5 and 1 mm in thickness were made by pressing YSZ powders in 1 inch diameter dies and sintering to full density at 1400°C in air. Anode compositions identical to those used in thin-film cells were prepared as described above, deposited onto the thick YSZ plate and fired on under reducing conditions in 4% H2 at 1350°C. Platinum reference electrodes and platinum cathodes were screen printed onto the YSZ plate and fired on in air at 900°C in the geometry shown below in Figure 4. Strontium titanate was obtained from Aldrich and milled to size, while doped strontium titanate materials were synthesized using combustion synthesis from the metal nitrates in glycine solution (6).

![Diagram of Thick YSZ Cells](attachment:image.png)

**Figure 4. Thick YSZ cells used to determine anode overpotential as a function of interlayer composition.**

Platinum mesh current collectors were bonded to anode, cathode, and reference electrodes using Pt paste, and Pt wires were spot-welded to the Pt mesh; 2-wire connections were used for anodes and cathodes to eliminate IR drop in the leads. Metal supported cells were treated in the same manner. Electrode and electrolyte-supported cells were then sealed to alumina tube test rigs with Aremco cement and tested in an H2-H2O/air fuel cell environment.

**RESULTS AND DISCUSSION**

Through careful control of particle size, the sintering rates of the FeCr metal support, Ni-YSZ interlayer, and YSZ thin film can be adjusted to yield high quality electrode supported cells. Fracture of the metal supported cells for SEM examination is
exceedingly difficult due to the high strength of the FeCr support and its ability to deform plastically; this characteristic of the FeCr supported cell should prevent catastrophic failure of the stack, a common problem in ceramic supported stacks subjected to stresses during thermal cycling. In Figure 5 below, the desired microstructure is shown; a high strength porous FeCr support followed by a thin, porous Ni-YSZ electrode and a dense YSZ thin-film electrolyte. In some cases, an additional layer of LaCrO$_3$ is used between the FeCr and Ni-YSZ to prevent diffusion of Cr into the Ni electrode. In some cases we have also introduced YSZ fibers in the formulation of the Ni-YSZ interlayer to maintain high porosity.

![Figure 5. SEM of fracture-section of stainless steel supported SOFC.](image)

The performance of two FeCr supported cells is shown in Figure 6. One of the metal supported cells includes YSZ fiber in the Ni-YSZ interlayer while the other cell has a thin layer of LaCrO$_3$ (~10 to 20 μm) between the FeCr support and the Ni-YSZ electrode. This is done to prevent diffusion of Cr into the Ni electrode during sintering at 1350°C. As can be seen in Figure 5, the metal supported cells were fabricated with platinum cathodes; since Pt does not have a particularly low overpotential for oxygen reduction,
there is some penalty in performance. As can be seen from Figure 6, the performance of the metal supported cells is reasonable; at 800°C the cell containing the LaCrO$_3$ film attains a power density of about 180 mW/cm$^2$ and at 900°C about 350 mW/cm$^2$. These cells Metal supported cells having LaCrO$_3$ interlayers have shown the highest levels of performance to date, possibly due to prevention of Cr diffusion into the Ni during sintering.

![Figure 6. Performance of metal supported SOFCs in H$_2$-H$_2$O/air at 800 and 900°C.](image)

Metal supported SOFCs were also formulated using SrTiO$_3$-NiO-YSZ interlayers. However, upon examination of the fracture sections of the metal supported cells, it was seen that strontium titanate sinters rapidly at 1350°C under reducing conditions. Consequently, if strontium titanate anodes are to be used in metal supported cells, control of the densification of the interlayer for co-fired cells will be an important issue.

![Figure 7. SEM of fracture cross-section of FeCr/SrTiO$_3$-Ni-YSZ/YSZ thin-film cell sintered at 1350°C in 4% H$_2$.](image)
As can be seen in Figure 7, the SrTiO$_3$-YSZ-Ni interlayer has sintered to near full density, and consequently is unsuitable as an electrode. If this can be corrected through the use of sintering inhibitors, SrTiO$_3$-based interlayers may be an attractive option for metal based cells due to their tolerance to sulfur, chemical compatibility with FeCr alloys, and low overpotential for hydrogen reported in the literature.

Electrode Kinetics Studies

In order to determine which electrode composition is suited for use as an interlayer for metal supported SOFCs, we studied determine the overpotential for a variety of interlayer compositions using electrolyte supported cells as shown in Figure 4, sintered under the conditions encountered during co-firing. A variety of anode compositions were used including NiO-YSZ, SrTiO$_3$, SrTiO$_3$ + 5 wt% NiO, Sr$_{0.85}$Ti$_{0.95}$Y$_{0.1}$Co$_{0.05}$O$_3$, and the composition reported by PNNL, La$_{0.65}$Sr$_{0.35}$Ti$_{0.8}$Ce$_{0.2}$O$_3$ (CeO$_2$ present as 2nd phase). The overpotential of the various electrodes was determined through the use of a Pt reference as shown in Figure 4, and the data corrected for IR drop across the YSZ electrolyte.

![Figure 8. Anode overpotential at 800°C in H$_2$-H$_2$O as a function of composition for electrodes sintered at 1350°C in 4% H$_2$.](image)

As would be expected, NiO-YSZ anodes sintered in air show low overpotential at 800°C (Figure 8). The effect on performance for sintering the NiO-YSZ anode in 4% hydrogen is minimal as the overpotential data in Figure 8 show. The performance of SiTiO$_3$ anodes is poor as evidenced by the large polarization at low current density. However, addition of only 5 wt% NiO to SrTiO$_3$ improves greatly the performance of the titanate based...
anode. We also examined the behavior of the doped \( \text{La}_{0.65}\text{Sr}_{0.35}\text{Ti}_{0.8}\text{Ce}_{0.2}\text{O}_3 \) anode described by PNNL. Although the performance of this material was superior to \( \text{SrTiO}_3 \), it did not match the performance reported by PNNL; this may be due to differences in composition or microstructure of the LBNL \( \text{La}_{0.65}\text{Sr}_{0.35}\text{Ti}_{0.8}\text{Ce}_{0.2}\text{O}_3 \) anode. However, if the low overpotential for \( \text{La}_{0.65}\text{Sr}_{0.35}\text{Ti}_{0.8}\text{Ce}_{0.2}\text{O}_3 \) can be duplicated, this may be an excellent choice for metal supported systems. In order to determine the effect of Cr diffusion into the Ni electrode we also fabricated a variety of Ni-YSZ based anodes that were fired at 1350°C in 4% \( \text{H}_2 \); 1) NiO-YSZ; 2) NiO-YSZ/FeCr 3) NiO-YSZ/\( \text{LaCrO}_3/\text{FeCr} \); and a NiO-YSZ anode fired in air and reduced \textit{in situ}.

![Figure 9. Overpotential for Ni based anodes fired under reducing and oxidizing conditions.](image)

As can be seen from Figure 9, the overpotential for Ni-YSZ is essentially unchanged by firing in a reducing environment. However, there is a significant penalty for processing the Ni-YSZ anode in the presence of FeCr at 1350°C, where interdiffusion of Cr, Fe, and Ni should be fairly rapid. The use of a \( \text{LaCrO}_3 \) as a barrier layer improves the anode overpotential, presumably is preventing interdiffusion.

**CONCLUSIONS**

The use of porous ferritic steel as a structural support for thin-film solid oxide fuel cells greatly reduces the cost of raw materials in the SOFC stack, and may aid the introduction of cost-effective systems. Proof of principle has been demonstrated using commercial
446 alloys and a catalytic interlayer, typically composed of Ni-YSZ. Half-cell measurements have shown that the overpotential for Ni-YSZ electrodes is increased by exposure to FeCr during high temperature firing in hydrogen. In order to match the performance of Ni-YSZ supported cells, it is likely that a barrier layer to metal interdiffusion, or lower temperature processing will be necessary. Preliminary measurements have indicated the use of a LaCrO3 barrier layer improves the performance of FeCr supported cells. The use of titanate based anodes may also avoid the problem of metal diffusion into the anode interlayer. So far, half-cell measurements made by our group have shown relatively large overpotentials for doped SrTiO3 anodes such as La0.65Sr0.35Ti0.8Ce0.2O3, but other groups have reported excellent performance for these materials (5). The use of metal-supported cells also increases the strength of the thin-electrolyte design greatly, which should translate to greater flexibility in stack design.

ACKNOWLEDGMENTS

This work was supported by Ikerlan Corporation in Minano, Spain and by the U.S. Department of Energy, through the National Energy Technology Laboratory, under Contract No. DE-AC03-76SF00098.

REFERENCES

1. S. C. Singhal, in Solid Oxide Fuel Cells VI, S. C. Singhal and M. Dokiya, Editors, PV 99-19, p. 39, The Electrochemical Society Proceedings Series, NJ (1999).

2. S. De Souza, S. J. Visco, and L. De Jonghe, "Reduced-temperature solid oxide fuel cell based on YSZ thin-film electrolyte," J. Electrochem. Soc., 144, L35-L37 (1997).

3. N. Minh, A. Anumakonda, B. Chung, R. Doshi, J. Ferrall, J. Guan, G. Lear, K. Montgomery, E. Ong, and J. Yamanis, in Solid Oxide Fuel Cells VI, S. C. Singhal and M. Dokiya, Editors, PV 99-19, p. 68, The Electrochemical Society Proceedings Series, NJ (1999).

4. G. Schiller, R. Henne, M. Lang, S. Schaper Deutsches Zentrum fur Luft und Raumfahrt (DLR) Pfaffenwaldring 38-40, D-70569 Stuttgart, Germany, in Solid Oxide Fuel Cells VI, S. C. Singhal and M. Dokiya, Editors, PV 99-19, p. 893, The Electrochemical Society Proceedings Series, NJ (1999).

5. O. A. Marina, and L. R Pederson, in the proceeding for the Fifth European Solid Oxide Fuel Cell Forum, p. 481, Lucerne Switzerland, July 1-5, 2002.

6. L. A. Chick, L. R. Pederson, G. D. Maupin, J. L. Bates, L. E. Thomas, and G. J. Exarhos, Mater. Lett., 10, (1-2), 6-12 (1990).