Rapid Thermal Cycling of Metal-Supported Solid Oxide Fuel Cell Membranes

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Abstract

Solid oxide fuel cell (SOFC) membranes were developed in which zirconia-based electrolyte thin films were supported by a composite metal/ceramic electrode, and were subjected to rapid thermal cycling between 200 and 800\(^\circ\)C. The effects of this cycling on membrane performance were evaluated. The membranes, not yet optimized for performance, showed a peak power density of 350mW/cm\(^2\) at 900\(^\circ\)C in laboratory-sized SOFCs that was not affected by the thermal cycling. This resistance to cycling degradation is attributed to the close matching of thermal expansion coefficient of the cermert support electrode with that of the zirconia electrolyte.

Key Words: thin film SOFC, metal support electrodes, thermal cycling, fast response.

1. Introduction

An essential characteristic of solid oxide fuel cell (SOFC) membranes designed for distributed stand-by power or for auxiliary power units (APUs) is their ability to withstand rapid thermal cycles. A first requirement of such fuel cell systems is a
sufficient power density at intermediate operating temperatures. A second requirement is that the membrane materials be compatible, both during fabrication and during use. A third requirement is that such fuel cell systems can be brought into operation rapidly from ambient temperatures, preferably in a matter of minutes. Economic considerations also impose the use of intrinsically low-cost materials. Numerous authors have reported meeting the power requirements at reduced temperatures through the use of anode-supported thin film solid oxide fuel cell membrane.

The requirement of significant cost reduction as well as robustness of the membranes has prompted the exploration of alternative membrane architectures in which the structural and the catalytic functions of the supporting porous electrode are separated. While in the past, cheap steel alloys has been used only as current interconnects. In our new configuration, a porous metallic alloy provides the mechanical support for the electrolyte film, and serves as the electrical connection, while the electrocatalytic function is maintained by a thin (10-15 µm) layer of Ni/zirconia adjacent to the solid electrolyte/electrode interface.

A remaining issue – particularly important in the context of intermittently operating systems – is the capability of the fuel cells to withstand not only repeated but also rapid thermal cycling. There are, as yet, no fully satisfactory answers to reliability questions for solid oxide fuel cells in intermittent distributed power scenarios. The basic problem is one of materials compatibility. The present work seeks to remedy this problem through the identification and evaluation of metal alloy/ceramic (cermet) electrode materials that can support a thin-film solid oxide electrolyte, without causing failure of the SOFC membrane during rapid thermal cycling.
A thin ceramic electrolyte film (10-30 micrometers) is essential for lowering the operating temperature of SOFCs from the usual ~1000°C to 650-800°C. Reduction of the operating temperatures to below 800°C offers the possibility of using metallic interconnects without their excessive oxidation, while still allowing for direct reforming of hydrocarbons, and for some practical forms of cogeneration. In a typical SOFC membrane configuration, a porous composite Ni/Yttria Stabilized Zirconia (YSZ) anode, 1 to 2 mm thick, supports the zirconia-based electrolyte film. However, this Ni/YSZ anode layer can add significant cost due to its needed high volume fraction of zirconia. In addition, the Ni/YSZ electrode is mechanically rather fragile. Employing ferritic FeCr alloys as a the major mechanical support for the SOFC membrane not only reduces materials costs significantly, but also adds greatly to the mechanical robustness of the membrane. While the thermal expansion of these alloys can be close to that of the yttria or scandia-doped zirconia electrolyte, a complete match is necessary for rapid thermal cycling. This matching was achieved by dispersing a compatible, low thermal expansion ceramic into the FeCr alloy to form the support electrode.

The SOFC multi-layered membrane must also satisfy chemical compatibility of the various functional layers and reach sufficient area-specific power density. Electrodes must have high electronic conductivity and appropriate, stable porosity to minimize Ohmic and mass transport overpotentials. To meet those requirements metal-supported multi-layered SOFC membranes with the general architecture shown in Fig. 1, were produced and tested. The response to extensive rapid thermal cycling of these membranes was evaluated in a fuel cell configuration, before and after thermal cycling at approximate rate of 50°C/min between 200 and 800°C. Such cooling and heating rates
are actually more severe than could reasonably be expected in distributed power
generation scenarios but approach the requirements for APUs (50-100°C/min).

2. Experimental

Synthesis of starting materials

To minimize the ceramic content of the ferritic alloy used here, i.e. FeCr
containing 30 wt% chromium (Fe30Cr), addition of a near-zero coefficient of thermal
expansion (CTE) material would be ideal. A candidate material was Aluminum Iron
Titanate (AFT, Al1.57Fe0.43TiO5) with a CTE of less than 0.2 x 10^-6 K^-1 17, 18. Assuming a
simple rule of mixtures, only 5 vol% of AFT would be needed to produce a cermet that
fully matches the CTE of an 8YSZ electrolyte. In contrast, a complete CTE match
through addition of alumina (CTE ~ 8.5 x 10^-6 K^-1) would require as much as 30 vol% of
this ceramic, adversely affecting electronic conductivity, and increasing brittleness.
However, AFT is unstable in the reducing atmospheres necessary for the co-firing
process used here to make the SOFC membranes, decomposing into aluminum titanate
(AT) and iron. Aluminum titanate was therefore chosen as the ceramic additive. AT
also has a very low CTE (~ 0.5 x 10^-6 K^-1) 19. To match the thermal expansion of the YSZ by
using AT rather than AFT in the Fe30Cr alloy, the amount of ceramic additive needed to
be increased from 5 to only 6% by volume (~3 wt%).

Two different routes were followed to prepare the AT compound. A first route
was by a solid-state reaction between alumina, titania, and iron oxide powders. The
component oxide powders were mixed in the appropriate proportions (50.1, 49.9 of
Al2O3, TiO2 by weight % respectively), milled together in acetone in an attritor mill, and
calcined at 1300°C in an oxidizing atmosphere. This AT powder was re-milled in an
attritor mill, in acetone, for 3 hours, at 550 rpm. Subsequently, the AT powder was dried under a heat lamp, passed through a 25µm sieve, and mixed with Fe30Cr powder with a particle diameter between 38 and 75µm, to make the Fe30Cr3AT cermet, i.e. Fe30Cr containing 3wt% of AT. 1” diameter disks were prepared from this cermet powder by die-pressing at 10,000psi, and firing at 1350°C in a reducing atmosphere.

A second method for preparing the low expansion additive was a sol-gel process. The gel was prepared from titanium butoxide (Aldrich Chemical Company, Inc) and aluminum nitrate (Alfa Aesar) (1:1 by weight Al nitrate and Ti butoxide). 5g of the solids were mixed into 20 ml isopropanol, in a nitrogen protective environment. The as-prepared sol-gel was then mixed with the Fe30Cr alloy powder, and dried under heat lamp for 6 hours.

Fabrication of cermet support layer

The porous Fe30Cr3AT cermet support layers were fabricated following two different processing methods. Method A included a pre-firing of the porous cermet layers in a reducing atmosphere, while method B involved a pre-firing in an oxidizing atmosphere (ambient air). The method of addition of the AT was the same in method A and B. In contrast to the sol-gel prepared AT, addition of the solid-state prepared AT did not lead to a satisfactory distribution of this low expansion additive, and was not pursued further.

Method A

Fe30Cr3AT powder was mixed with 3wt% Carbowax binder dissolved in isopropanol (1g Carbowax in 20 ml of isopropanol). The slurry then was dried under a heat lamp, for 4h, at 120°C. The dried powder was passed through a 100 µm sieve with opening, and
die-pressed at 10,000 psi, in 1” diameter steel die, to form the support layer of the SOFC membrane. The pressed disks were pre-fired in a reducing atmosphere of 4% H₂ in Argon, at 900°C, for 2 hours. This pre-firing gave enough strength to the cermet for the subsequent manipulations involved in the integration of the additional functional layers (shown in Fig. 1).

**Method B**

The Fe30Cr3AT powder was mixed with 5 wt% stearic acid dissolved in acetone binder by weight, and dried under heat lamp, for 20 min, at 80°C. The dried powder was sieved through a 100 µm sieve, and die pressed into the 1” diameter disks, at 10,000 psi. The disks were pre-fired in oxidizing atmosphere at 400°C. This low temperature pre-firing step in oxidizing atmosphere gave sufficient strength to the disks, similar to one obtained in method A. In this case, the strength of the disk was due to the low-temperature oxide formation, bonding the metal particles. Surface oxidation of these pre-fired metal disks was evidenced by their discoloration, attributed to the formation of chromium oxide and iron oxides.

**Integration of Ni/YSZ catalytic layer**

The porous Ni/YSZ catalyst layer was deposited on the pre-fired Fe30Cr3AT cermet support electrode, either by modified tape casting or by screen-printing. Mixtures of YSZ and NiO (45 and 45 wt %), polyvinyl butyral (PVB) and polyethylene glycol (5 and 5 weight %), were suspended together in the isopropanol and milled in an attritor mill, for three hours, at 550 rpm. Then, the attritor-milled slurry used for the NiO/YSZ layer was applied by either tape casting or screen printing, and the samples
were pre-fired at 500 °C, in ambient atmosphere, to achieve binder burnout, leaving an adherent, porous NiO/YSZ layer. The surface of the deposited NiO/YSZ layer was smooth, and showed no visible flaws at 200X magnification. For high substrate porosities, it was necessary to increase the NiO/YSZ slurry viscosity by increasing solids loading until the slurry no longer penetrated the porous substrate, forming a smooth layer on which the electrolyte layer would be deposited.

**Application of the YSZ electrolyte film**

The YSZ electrolyte film was applied following three different methods: tape casting, vacuum infiltration of a colloidal suspension, or colloidal spray-deposition. Tape casting of the YSZ film was similar to the application of the Ni-YSZ catalytic layer. However, the densification and thickness of the electrolyte deposited by tape casting was inferior to that of the other two techniques.

The vacuum infiltration setup is shown schematically in Fig. 2. The colloidal suspension consisted of 0.8g/liter of YSZ powder (Tosoh Corporation), with an average diameter of 0.35µm, suspended in isopropanol by ultra-sonicating for 4 min. The substrate (porous Fe30Cr3AT cermet disc with the pre-fired Ni/YSZ catalytic layer) was affixed to the vacuum line, and immersed into the YSZ colloidal suspension, as shown in Fig. 2. Both the suspension concentration and the immersion time, typically 5 min, determined the thickness of the colloidal YSZ deposit. The process in some respects resembles slip casting, but the suspension is much less concentrated compared to regular slip casting. High solids loading in colloidal vacuum infiltration makes control of the deposit thickness very difficult, and is thus to be avoided. To manage shrinkage of the YSZ electrolyte the green density of the deposited film needs to be carefully controlled.
The density of the as-deposited YSZ layer was affected by the nature of the solvent. YSZ suspensions in alcohol led to at least 3% less film linear shrinkage compared to water-based suspensions. However, the water-based process required very slow drying (as much as 5 hours at room temperature), to avoid film drying cracks. The vacuum infiltration technique requires the surface of the porous substrate layer to be highly uniform, with substrate pores no larger than about 3-5 times the powder agglomerate diameter. Additionally, accidental inclusion of organic or inorganic dust particles may introduce pinholes in the sintered electrolyte, and must be avoided. Increasing the thickness of the YSZ film can in part compensate for the deleterious presence of larger pores or other imperfections exceeding this tolerance, but this leads to an excessive electrolyte resistance.

For colloidal spray-deposition, YSZ powder (Tosoh) was suspended in isopropanol at 5g/liter. Spray-deposited green film properties could be modified by binder addition (PVB or Carbowax binders). Addition of 10 to 20 vol% of binder increases the strength of the green film, making it potentially possible to build thicker YSZ electrolyte films without the cracks that otherwise could develop due to excessive drying stresses. However, suspension modification by such binder addition invariably led to agglomerate formation, and was not a successful strategy for obtaining continuous thin green films. For spray-deposition, YSZ/isopropanol suspensions without binder altogether yielded the best, smooth and flawless green films. After co-firing of the multilayer SOFC membrane at 1350°C, in reducing atmosphere, for 4 hours, the resulting YSZ electrolyte film was dense and free of pinholes and electronic shorts.
Vacuum infiltration and spraying depositions led to a similar quality of electrolyte films, but spraying was a more convenient technique for the lab-prepared SOFC.

The sintered membranes were sealed onto an alumina tube with Ceramabond 571-p and Ultra-Temp-516 sealing compounds from Aremco Products, Inc. Subsequently, LSCF (La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.8}FeO\textsubscript{3}), prepared by the GNP (Glycine Nitrate Process) described elsewhere\textsuperscript{20} was used for producing functioning cathodes. The cathode was sprayed onto the YSZ electrolyte of the co-fired membrane, and sintered at 900°C.

**Electrochemical testing**

Current-voltage (I-V) measurements of the Fe30Cr3AT- supported cells were made using a Princeton Applied Research potentiostat Model 371, at a current rise rate of 15mA/min. In addition, the AC impedance was also recorded, showing results in agreement with I-V characteristics.

**3. Results and discussion**

**Thermal expansion measurements**

To determine the thermal expansion of YSZ, Ni-YSZ, Fe30Cr, and Fe30Cr3AT, dilatometer measurements were made. Pellets (4 mm diameter and 25.4mm thickness) of the various powders were die-pressed at 10,000psi, and heated in an Orton dilatometer (Model 1600). The thermal expansion of the AT was negligible compared to that of the Fe30Cr alloy. The thermal expansion of the materials was recorded between room temperature and 1200°C and is shown in Fig. 3.
The dilatometer studies showed that thermal expansion of the metal/ceramic composite substrate was matched fully with that of the 8YSZ electrolyte.

**Cermet support layer microstructure**

The low-CTE additive distribution in the metal substrate and microstructure of the fuel cell support were studied using SEM. The porous metal support layer prepared by sol-gel incorporation of AT (alumina titanate) into the Fe30CR powders showed a uniform distribution of the near-zero thermal expansion compound between the ferritic alloy grains as shown in Figs. 4.

Attempts to use LSM (LaSrMnO$_4$) as a cathode in the co-fired structure were not successful. LSM is not stable in reducing atmosphere needed for co-firing. Moreover, attempts to form LSM cathodes *in situ* during the heat-up of the SOFC test rig did not to lead to a usable cathode. In contrast, LSCF sinters at lower temperature and these cathodes could be fired at 900 °C for 1 hour. Cross sections of complete Fe30Cr3AT-supported fuel cell membranes are shown in Fig. 5 and 6. It is important to note that the thin electrolyte YSZ film appeared fully dense, without any noticeable pores. It is also evident that the colloidal spraying method for electrolyte deposition described above allows for excellent control over the film thickness to within ±2µm for a 20 µm thick electrolyte film. The Ni- containing catalytic layers appeared sufficiently porous to support adequate fuel supply. Overall, the structure of the layered electrodes (the Fe30Cr3AT anode support layer, and the LSCF cathode in Fig. 6 appear to be sufficiently porous, and thus overpotentials due to mass transport could be expected to be relatively low during operation of the fuel cells.
Thermal cycling

To evaluate the effects of thermal cycling, the Fe30Cr3AT supported fuel cell membranes were cycled 50 times between 200 and 800°C, in 4%H₂/nitrogen, at heating and cooling rates of approximately 50°C/min. SEM images showed no cracking or delamination of the multilayered SOFC membranes.

Current/voltage (I-V) testing of the fuel cell membranes

Typical I-V curves for the membranes before and after thermal cycling are shown in Fig. 8. It is clear that the thermal cycling did not affect the performance of these membranes. At 900°C, both samples show a maximum power density of about 350 mW/cm², with similar I-V responses. The use of a better cathode catalyst would likely improve cell performance. These results indicate that the close thermal expansion matching of porous metal cermet support electrodes to that of the zirconia electrolyte can be successful in eliminating the deleterious effects of rapid thermal cycling on SOFC membranes performance.

4. Conclusions

SOFC membranes were prepared in which the thin zirconia electrolyte film is supported by a porous ferritic alloy layer of which the thermal expansion coefficient has been manipulated by the addition of 6 vol% aluminum titanate. The compatibility of the various membrane layers during the processing has been shown. The ability of the cermet supported thin film SOFC membranes to withstand rapid thermal cycling between 200
and 800°C at 50°C/min has been demonstrated. Testing of the SOFC membranes in laboratory cells showed a peak power density of 350mW/cm² at 900°C.

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References


Figure Captions

Fig.1 General architecture of the multi-layered fuel cell membrane.

Fig.2 Schematic for YSZ vacuum infiltration deposition.

Fig3. Thermal expansion of 8YSZ electrolyte, Ni/8YSZ anode, Fe30Cr alloy, and Fe30Cr-6AT.

Fig. 4. Scanning electron microscope image of a polished cross section of the cermet support. Distributed particles of AT may be discerned. The dark areas are the mounting epoxy needed to allow polishing.

Fig 5. Fracture cross-section of Fe30Cr+6AT supported SOFC electrolyte layer after co-firing at 1350°C.

Fig. 6. Fracture cross section of a complete Fe30Cr+6AT-supported SOFC membrane after firing at 1300°C.

Fig. 7. Power density and polarization of the Fe30Cr+6AT supported fuel cell with LSCF cathode before and after thermal cycling at 900°C.
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Polarization and power density of the cell with LSCF cathode at 900°C.

Fig. 7  Power density and polarization of the Fe30Cr+6AT supported fuel cell with LSCF cathode before and after thermal cycling at 900°C.