FABRICATION AND PERFORMANCE OF THIN-FILM YSZ SOLID OXIDE FUEL CELLS BETWEEN 600 AND 800°C

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ABSTRACT

A new technique for the fabrication of yttria stabilized zirconia (YSZ) films on porous NiO-YSZ and LSM-YSZ composite substrates using aqueous YSZ-powder suspensions has been developed. The technique has been used to fabricate planar thin-film YSZ fuel cells. After sintering, the YSZ electrolyte thickness is between 3 and 10 μm, and the electrolyte is strongly bonded to the NiO-YSZ and LSM-YSZ substrates. The power density of the Ni-YSZ/YSZ/LSM-YSZ cell is over 0.8 W/cm² at 800°C. Initial investigations of doped-YSZ mixed-conducting electrodes in our thin-film YSZ cells indicate that Tb- and Ti-doped YSZs increase power densities from 15% to 50% at 800°C. New Cu-CeO₂-YSZ anodes for the dry oxidation of methane are also being developed.

INTRODUCTION

The high operating temperature (~ 1000°C) of tubular solid oxide fuel cells (SOFCs) is necessary to attain reasonable power densities. However a high operating temperature can introduce a number of complex materials problems, such as electrode sintering, interface diffusion between electrolyte and electrode materials, mechanical stresses due to the different thermal-expansion coefficients and high cost of ceramic interconnect materials (1). Thus many current research and development programs are focused on reduced-temperature (600 – 800°C) planar SOFCs. Cell-operating temperatures are reduced by using a thin-film YSZ electrolyte, and new electrode materials and designs to minimize cell-resistance and polarization losses.

Although the oxygen-ion conductivity of yttria-stabilized zirconia (YSZ) is not as high as that of other oxides such as doped ceria and doped lanthanum gallate (2, 3, 4), it is the preferred electrolyte due to its optimal combination of electrochemical and chemical stability and mechanical properties. Approaches for fabricating thin-film YSZ electrolytes include electrochemical-vapor deposition, sputter coating, sol-gel, tape calendering and dip coating (5-11). Although high quality thin-film YSZ electrolytes have been obtained, it is necessary to decrease thin-film YSZ fabrication costs and the high sintering temperatures. Most reported cell-fabrication techniques include sintering...
the YSZ electrolyte at high temperatures (typically 1400°C) on a NiO-YSZ substrate. (8, 9, 10). Such high sintering temperatures have prevented the development of cathode-supported YSZ thin-film cells and composite anodes for the dry oxidation of hydrocarbon fuels (12) in reduced-temperature SOFCs.

The current cathode and anode for thin-film YSZ SOFCs at reduced temperatures is a LSM-YSZ composite and a Ni-YSZ composite, respectively. Performance of these composite electrodes is limited because the electrode reactions are restricted geometrically to the three-phase-boundary (TPB) regions. Recent developments of improved electrode materials and designs have resulted in some improvements in cell performance. For example, changes in the Ni-YSZ composite anode design has resulted in significant increases in cell performance (10). It has also been reported that mixed-conducting materials such as terbia-doped YSZ (YZTb) (13 – 16), titania-doped YSZ (YZTi) (14 - 18), and yttria-doped ceria (19) can significantly lower electrode-overpotential losses.

In this paper we first summarize the performance at 600 to 800°C of Ni-YSZ supported thin-film YSZ cells fabricated using our new low-cost thin-film fabrication technique (20). Then we discuss some results from thin-film YSZ cells having cathodes containing mixed-conducting YZTb and anodes containing mixed-conducting YZTi. Our initial results with Cu-CeO2-YSZ composite anodes for the dry oxidation of methane are also reported.

**EXPERIMENTAL**

**Fabrication of Porous Electrodes and YSZ Thin-Film Electrolyte**

The 8%mol YSZ (Tosoh Ceramics), NiO (T. J. Baker) and LSM (La0.89Sr0.1MnO3) (Praxair) powders are used as received. The Y12ZTi20 (12Y2O3-20TiO2-68ZrO2) and Y6ZTb30 (6Y2O3-30TbO1.75-64ZrO2) mixed-conducting powders are prepared by co-precipitation using TiCl4 (Aldrich), Tb(NO3)3.5H2O, Y(NO3)3.6H2O and ZrOCl2.8H2O (Johnson Matthey). After annealing at 900°C for 5 hours, the ball-milled Y12ZTi20 and Y6ZTb30 have a single cubic phase and a particle size between 0.1 and 0.5 μm.

In our cell fabrication technique (20) the NiO-YSZ and LSM-YSZ (1:1 weight ratio) tape-cast green tapes are cut to desired size, and annealed in air (1000–1050°C for 1 hr) to obtain porous substrates with a thickness between 200 and 250 μm. The YSZ thin-film electrolyte is fabricated by depositing a YSZ-water suspension on substrates under controlled conditions and annealing at elevated temperature.

**Ni-YSZ Anode Supported YSZ Thin-Film Cells**

The YSZ thin-film electrolyte is deposited on the NiO-YSZ substrate and sintered at 1400°C for 4 hrs. A LSM-YSZ-glycerol slurry is then painted on top of the YSZ thin film and annealed in air. After the cell has been fabricated, Pt paste (A3788 Engelhard) is first applied on both electrode surfaces and annealed, and then Pt lead wires are applied to the electrode surfaces. Mixed-conducting Y12ZTi20 powder (~0.6mg/cm²) has been deposited on the porous NiO-YSZ substrate in one cell before the YSZ powder is
deposited. The NiO-YSZ, Y12ZTi20/YSZ anode-electrolyte is first sintered in air, and the LSM-YSZ (1:1 wt. ratio) cathode is then applied as stated above to make the Ni-YSZ, Y12ZTi20/YSZ/LSM-YSZ cell. Another cell has been prepared by depositing mixed-conducting Y6ZTb30 powder (~0.1 mg/cm²) on the thin-film YSZ electrolyte and annealing before the LSM-YSZ cathode is applied. A cell having a LSM-Y6ZTb30 composite cathode has also been prepared by painting a LSM-Y6SZTb30-glycerol slurry on the YSZ surface of a NiO-YSZ/YSZ bilayer, and then annealing.

**Fuel Cell Experiments and Microscopic Observations**

The thin-film YSZ cells are mounted on alumina tubes and sealed with Aremco cements. Hydrogen with ~ 3% H₂O is the fuel gas, and ambient air is the oxidizer. Cell measurements are conducted between 600 and 800°C, and cell performance is determined using a constant current measurement technique. Currents are increased in 20 mA increments and held for 10 minutes, and the experiment is terminated when the cell voltage drops below 0.3 volts. The Solartron 1286/1250 controlled by a HP-9000 computer is used for these and the cell-resistance measurements. The cell resistance is measured using AC impedance in the frequency range of 65 kHz to 0.1 Hz with a four-electrode configuration to eliminate the platinum-lead resistance. The YSZ electrolyte surface morphology and cell-fracture cross sections are observed using gold-coated specimens and a Jeol 6300FV scanning electronic microscope.

**Cu-CeO₂-YSZ Anodes for the Dry Oxidation of Methane (CH₄)**

Our initial experiments for new anodes for the dry oxidation of methane and other hydrocarbon fuels have used thick YSZ electrolytes (230 μm, prepared by tape casting). A LSM-YSZ cathode is painted on the YSZ electrolyte and annealed. Ni-CeO₂-YSZ and Cu-CeO₂-YSZ (40 wt.% Ni or Cu, 20 wt.% CeO₂) anodes are prepared using the same procedures (21, 22). After Pt current collectors are attached, cells are mounted on an Al₂O₃ tube sealed with quartz powder. The current-voltage characteristics have been determined at 800°C using dry H₂ and dry CH₄ as fuels. The cell voltage is maintained at 0.5 volts while monitoring the current density. The compositions of product gases leaving the cells are measured using a gas chromatograph.

**RESULTS AND DISCUSSION**

Thin-film YSZ has been deposited on NiO-YSZ and LSM-YSZ substrates using a YSZ-water suspension under controlled conditions. After sintering at temperatures between 1200°C and 1400°C in air for 4 hrs., dense thin-film (3 and 10 μm) YSZ electrolytes are obtained. The three scanning electron micrographs (SEMs) in Fig. 1 show the dense thin-film YSZ layers formed on the NiO-YSZ and LSM-YSZ substrates. These SEMs indicate that the higher the sintering temperature, the larger the grain size of the thin-film YSZ. The densification temperature of ceramics is highly dependent on the particle agglomeration and chemical composition. In many particle-deposition processes, there are particle agglomerates whose sintering temperature is higher than that of individual particles (23). However if the particles are densely packed and the agglomerates are eliminated, the sintering temperature of ~ 0.09 μm zirconia particles has
been decreased to 1100°C (24). Unfortunately the typical sintering temperatures of thin-film YSZ are ~ 1400°C (8, 9, 10) because current thin-film fabrication techniques do not minimize particle agglomeration. However in our technique (20) we have the ability to minimize particle agglomeration during the coating and drying steps, and have reduced sintering temperatures to ~ 1200°C as shown in Fig. 1.

Figure 1. SEMs of thin-film YSZ electrolyte sintered at different temperatures for 4 hrs and on different substrates. A. 1400°C, NiO-YSZ Substrate; B. 1300°C, LSM-YSZ Substrate; C. 1200°C, LSM-YSZ Substrate.

Figure 2 shows the interfaces between a 3 μm thin-film YSZ electrolyte and the Ni-YSZ and LSM-YSZ electrodes in a Ni-YSZ anode-supported cell. The performance of this cell at temperatures between 800°C and 600°C is shown in Fig. 3. The maximum cell power density is 0.85, 0.42 and 0.16 W/cm² at 800, 700, and 600°C, respectively. Due to the thin-film (~3 μm) YSZ and the good microstructure near the electrode-electrolyte interfaces, the area specific resistance (ASR) is also very low (0.071 Ω.cm) at 800°C.
Figure 2. SEM micrograph of the cross section of a thin-film (3 um) YSZ cell

Figure 3. Performance of a thin-film YSZ cell at 800°C, 700°C, and 600°C

Charge-transfer reactions in the Ni-YSZ and LSM-YSZ electrodes cells are limited to the Ni-YSZ-gas and the LSM-YSZ-gas three-phase boundaries because the electronic conductivity in YSZ and the oxygen-ion conductivity in Ni and LSM are negligible. Mixed conducting doped-YSZs can significantly increase the charge-transfer reaction areas in YSZ-based fuel cells and decrease cell-overpotentials. However, doping of YSZ with multi-valent elements (e.g. Ti, Tb) can also decrease the oxygen-ion conductivity in doped YSZ (13, 14, 18). To examine the effects of mixed-conducting doped YSZ particles on cell-power densities, we have deposited small particles of Ti-doped YSZ (Y6ZTi20) on the Ni-YSZ anode to introduce mixed-conducting surfaces (n-type electronic and oxygen-ion) in the Ni-YSZ anode. We have also deposited small particles of Tb-doped YSZ (Y12ZTb30) on the thin-film YSZ surface of a Ni-YSZ/YSZ bilayer to
introduce mixed-conducting surfaces (p-type electronic and oxygen-ion) in the LSM-YSZ cathode.

The performance comparison (illustrated in Fig. 4) of a typical Ni-YSZ anode cell with a Ni-YSZ, Y12ZTi20 anode cell at 800°C indicates a 50% increase in cell-power density when mixed-conducting Y12ZTi20 is deposited on the Ni-YSZ anode. A similar performance comparison (illustrated in Fig. 5) of a typical LSM-YSZ cathode cell with a Y6ZTb30, LSM-YSZ cathode cell at 800°C indicates a 15% increase in cell-power density when mixed-conducting Y6ZTb30 is deposited on the thin-film YSZ surface next to the LSM-YSZ cathode. The large power-density improvement in the cell containing

![Figure 4](image-url)

**Figure 4.** Cell-performance comparison of Ni-YSZ, Y12ZTi20 anode with a Ni-YSZ anode in Ni-YSZ supported thin-film YSZ electrolyte cells.

![Figure 5](image-url)

**Figure 5.** Cell-performance comparison of Y6ZTb30, LSM-YSZ cathode with a LSM-YSZ cathode in Ni-YSZ supported thin-film YSZ electrolyte cells.
Y12ZTi20 is presumably due to the larger surface area of the Y12ZTi20-particles (deposited on a highly porous NiO-YSZ substrate) than that of the Y6ZTb30 particles (deposited on a uniform YSZ thin-film surface).

Figure 6 indicates that the cell-powder density at 800°C increases by 30% when YSZ in a LSM-YSZ composite cathode is replaced with mixed conducting (p-type electronic and oxygen-ion) Y6ZTb30 to form a LSM-Y6ZTb30 composite cathode. The advantage of a LSM-YZTb composite cathode over a LSM-YSZ composite cathode is that the charge-transfer reaction occurs over the entire surface area of mixed-conducting YZTb, which significantly lowers cathodic-polarization losses. There is a significant difference between the 15% improvement in the deposited Y6ZTb30-particle cathode shown in Fig. 5 and the 30% improvement in the LSM-Y6ZTb30 composite-cathode cell shown in Fig. 6. This improvement is presumably due to reduced cathodic-polarization losses because the 50 wt.% mixed-conducting Y6ZTb30 in the porous composite-cathode provides a larger Y6ZTb30-air interface area for the charge-transfer reaction.

![Figure 6. Cell-performance comparison of LSM-YSZ and LSM-Y6ZTb30 composite cathodes in Ni-YSZ supported thin-film YSZ electrolyte cells.](image)

The performance of the Ni-CeO2-YSZ and Cu-CeO2-YSZ anodes in H2 and CH4 at 800°C is shown in Fig. 7. The H2 fuel is changed to CH4 and then back to H2. The current density during the first 60 min. cycle for the Ni-CeO2-YSZ anode with H2 is approximately 235 mA/cm² (12). Upon changing to dry CH4, the current density initially increases slightly to 244 mA/cm² and then rapidly decreases to zero. Changing back to H2 has no effect. Post examination revealed carbon filaments filling the tube surrounding the anode. After a short induction period with H2, the Cu-CeO2-YSZ anode cell operated steadily at 200 mA/cm². Changing to CH4 decreased the current density to ~90 mA/cm², and the current then remained constant. When the fuel was changed back to H2, the current density returned to 200 mA/cm². The cell performance was stable over three days.
in dry CH$_4$. Post analysis of this anode showed no carbon deposition, demonstrating the stability of Cu- CeO$_2$-YSZ anode cells in dry methane.

Gas chromatography has been used to measure the effect of current density on the outlet-gas composition of a Cu-CeO$_2$-YSZ anode cell. Although traces of CO could be detected, CO$_2$ is the primary carbon product from the dry oxidation of CH$_4$. Figure 8 shows that the conversion of CH$_4$ increases linearly with current density, which is expected for direct Faradaic oxidation (12). Additional proof for the direct oxidation of

![Figure 7](image-url)

**Figure 7.** Variations of current densities for Ni- and Cu-based anodes in H$_2$ and CH$_4$ fuel in thick (230 µm) YSZ cells at 800°C

![Figure 8](image-url)

**Figure 8.** Comparison of measured and calculated methane conversion for dry oxidization of CH$_4$ with a Cu-CeO$_2$-ZrO$_2$ anode at 800°C
CH$_4$ comes from the agreement between the data points and the solid line calculated assuming that the total oxidation of CH$_4$ proceeds according to the following reaction:

$$
\text{CH}_4 + 4\text{O}^2^- \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 8\text{e}^-.
$$

**SUMMARY AND CONCLUSIONS**

A low-cost, particle-deposition technique has been developed to fabricate thin-film YSZ electrolyte fuel cells (20). The ability to minimize particle agglomeration during the coating and drying steps has reduced the thin-film YSZ sintering temperature to below 1300°C. The lower sintering temperatures permit using novel electrode materials that would be inoperable if exposed to higher sintering temperatures. The dense YSZ thin-films that have been formed on Ni-YSZ and LSM-YSZ porous substrates are between 3 and 10 μm thick.

The maximum cell-power densities of a typical anode supported Ni-YSZ/YSZ/LSM-YSZ cell (fabricated using our particle-deposition technique) are 0.85, 0.42 and 0.16 W/cm$^2$ at 800, 700, and 600°C, respectively (Fig. 3). Addition of mixed-conducting doped-YSZs (Y$_6$Z$_1$Tb$_3$O$_{30}$ and Y$_{12}$Z$_1$Tl$_2$O$_{20}$) particles to the typical composite electrodes increases the power densities of similar cells without these mixed conductors from 15 to 50% (Fig. 4 and 5). Initial studies of the direct oxidation of methane indicate that Cu-CeO$_2$-YSZ anodes are stable, and that the electrode reaction is a direct-oxidation process with no internal reforming.

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