Processing and Characterization of Sc$_2$O$_3$-CeO$_2$-ZrO$_2$ Electrolyte Based Intermediate Temperature Solid Oxide Fuel Cells

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ABSTRACT

ScCeZrO$_2$ ceramic powders produced by two different manufacturers have been used for the manufacturing of ScCeZrO$_2$ electrolyte based Solid Oxide Fuel Cells. Thin porous anode and cathode layers have been deposited on 150 µm thick dense electrolyte layers. Preliminary electrochemical testing of the produced cells has been performed.

INTRODUCTION

Fully stabilized zirconia is commonly used as an electrolyte material for solid oxide fuel cells (SOFC) due to its good oxygen conductivity at high temperatures (800-1000°C). Yttria stabilized zirconia (YSZ), in particular, has been used extensively in high temperature SOFCs [1]. Although the ionic conductivity of ceramics generally increases with higher temperatures, stability, reliability, and material costs can be improved by decreasing operating temperatures. For this reason, much attention is being given to electrolyte materials that exhibit high ionic conductivity in the intermediate temperature range. One such material is Sc$_2$O$_3$ stabilized ZrO$_2$ (ScSZ), which shows high conductivity in the 700-800°C range, in comparison with YSZ. The drawback of ScSZ is that it demonstrates an ordering of vacancies over time, called the aging phenomenon, accompanied by a phase transition to a lower symmetry rhombohedral phase, resulting in decreased conductivity [2]. However, when zirconia is stabilized with CeO$_2$ as well as Sc$_2$O$_3$, it no longer exhibits an unfavorable phase transition, making this material a very promising option for intermediate SOFC electrolytes [3]. The goal of this research, therefore, is to develop and test Sc$_2$O$_3$-CeO$_2$-ZrO$_2$ electrolyte based single cells.

EXPERIMENTAL PROCEDURE

Two different commercial powders, both with the nominal composition of 10 mol% Sc$_2$O$_3$ + 1 mol% CeO$_2$ + ZrO$_2$ (ScCeZrO$_2$), were compared for use as an intermediate temperature electrolyte material. One powder was manufactured by Praxair Surface Technologies, USA, using spray pyrolysis, and the other by Daiichi Kigenso Kagaku Kogyo Co., (DKKK), Japan, using co-precipitation technique. Although the nominal compositions of both powders were the same, inductively coupled plasma mass spectroscopy (ICP MS) has shown that the true compositions are 15% Sc$_2$O$_3$ + 0.05% HfO$_2$ + 0.4% CeO$_2$ + 2%TiO$_2$ + ZrO$_2$ for the Praxair powder, and 10.07% Sc$_2$O$_3$ + 0.92% HfO$_2$ + 1.03% CeO$_2$ + 1.4%TiO$_2$ + ZrO$_2$ for the DKKK powder [4].
For the cathode La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_3$ (LSFC) powder was mixed with 20 mol% Gd$_2$O$_3$ + CeO$_2$ (GDC) in a 50:50 wt% ratio. Both the LSFC and GDC powders were manufactured by Praxair Surface Technologies. 35 wt% NiO powder, manufactured by Novamet, USA, and 65-wt% ScCeZrO$_2$ were mixed together to form an anode powder using a ball mill with a grinding media of zirconia balls and acetone for 48 hours. The specific surface area (SSA), grain size distribution, and theoretical density ($\rho_{th}$) of the DKKK, Praxair, LSFC, GDC and NiO powders are presented in Table I. The theoretical densities were calculated by Rosten [5].

To characterize the sintering behavior of the ceramic materials used in this research, dense electrolyte, as well as porous cathode and anode samples were prepared. The powders were pressed uniaxially in a steel die at 20 MPa. The resulting compacts were sintered in air at varying temperatures and times. Sintering temperatures ranging from 1100°C to 1600°C in 100°C increments were compared for the electrolyte at a dwell time of 2 hours, using heating and cooling rates of 10°C/min. The anode and cathode compacts were sintered at temperatures ranging from 1000°C to 1150°C and 1100°C to 1500°C respectively for 2 hours, using heating and cooling rates of 1°C/min and 5°C/min respectively. The densities of the sintered samples were measured using the liquid immersion technique and their porosities were calculated using their respective theoretical densities. The shrinkage during sintering of these samples was recorded using a BAHR Dil802 dilatometer.

Slurries were prepared for tape casting using both DKKK and Praxair ScCeZrO$_2$ powders. The slurries, which consisted of 61.94 wt% oxide powder, 1.24 wt% menhaden fish oil, and 15.31 wt% of both xylenes and ethanol, were placed in a roll mill for 24 hours using zirconia pellets as a grinding medium. Next, 3.09 wt% polyvinyl butyral and 1.55 wt% each of butyl benzyl phthalate and polyalkylene glycol were added, and the slurry was again placed in the roll mill for 24 hours. Tapes were cast in thicknesses of 200 and 400 µm using a Richard E. Mistler full-scale tape casting machine. The ScCeZrO$_2$ tapes were laminated together in stacks of up to four layers, using 135 MPa in a uniaxial press. A sintering temperature of 1500°C was chosen for the laminated tapes, based on the porosities of the initial sintered compacts. After sintering, some electrolytes were fractured and an SEM was used to determine their final thicknesses and approximate porosities. The anode and cathode powders were made into inks using an Anthony 2.5” x 5” Three Roll Mill. The anode and cathode inks were printed onto either side of the sintered electrolytes using an Aremco Products accu-coat 3230 screen printer. The printed cathode and anode layers were about 5 µm thick after being sintered in air at 1100°C for 2 hours.

Completed button cells made with a DKKK electrolyte, a 35 wt% ScCeZrO$_2$ – 65 wt% NiO anode, and an 50wt% LSFC + 50wt% GDC cathode were tested at 800°C. Air was used on the cathode side, and a mixture of 97% hydrogen and 3% water was used on the anode side.
Mica was used to seal the cell between two alumina flanges. Current scans were used to determine cell performance.

**RESULTS AND DISCUSSION**

The techniques used for manufacturing of ScCeZrO$_2$ powders were different, and as a result, the morphology and properties, along with the chemical composition of the Praxair and DKKK powders differed significantly. SEM micrographs of Praxair and DKKK powders are shown in Figure 1. Praxair powders are presented as sintered platelet agglomerates, up to 300 µm in length and 30-40 µm thick, which consist of smaller 60-100 nm crystalline particles. DKKK particles are presented as soft spherical agglomerates with diameters of up to 100 µm, also consisting of 60-100 nm crystalline particles. These morphological features, along with differences in the chemical compositions of both powders resulted in significantly different sintering behaviors. Typical microstructure of DKKK ceramics sintered at 1600 ºC for 10 and 24 hours is shown in figure 2, a and b. The DKKK powders showed more active sintering behavior than that of Praxair, reaching 93-95% of theoretical density when sintered at 1300ºC for 2 hours. Comparatively, the Praxair powder required higher sintering temperatures, reaching 93-95% of theoretical density only after sintering for 2 hours at 1500ºC (Figure 3 and 4). The

**Figure 1.** Scanning electron microscopy of ScCeZrO$_2$ electrolyte powders; (a) Praxair powder platelets, (b) Praxair grains, (c) DKKK powder spheres, and (d) DKKK grains.

**Figure 2.** SEM images of DKKK ceramics sintered at 1600 ºC for (a) 10 h and (b) 24 h
measured porosities of pellets made from Praxair and DKKK ScCeZrO₂ powders, along with the composite LSFC+GDC cathode and the NiO+DKKK anode powders are presented in Figure 4. XRD of the DKKK and Praxair ScCeZrO₂ powders (Figure 5), and the GDC and NiO powders revealed no secondary phases. A mixture of rhombohedral and cubic phases has been detected at 1100°C and 1200°C in the DKKK ceramic, although at all other temperatures only pure cubic phase was found. A small amount of Co₂O₃ and SrCoO₂.₅₂ secondary phases were found in the LSFC.

Anode and cathode inks were successfully prepared using the three-roll mill, and electrolyte powders were tape cast and laminated in stacks. Curling was one major complication that occurred during sintering of the electrolyte tapes. This problem was partially solved by covering the tapes with a thick, uniform layer of coarse ScCeZrO₂ powder during sintering. This
reduced curling to a large extent for the DKKK tapes, but did not affect the Praxair tapes. Due to the DKKK powder’s better sintering characteristics and higher ionic conductivity of 0.151 S/cm at 800°C compared with 0.085 S/cm of Praxair, the DKKK tapes were used preferentially over Praxair for button cell manufacture. Anode and cathode inks were successfully screen printed and co-fired on a few DKKK electrolytes. Both green and sintered tapes, as well as a complete
button cell are shown in Figure 6 below. Cosintering of the screen-printed electrodes resulted in good adhesion to the electrolyte, and good porosity in the electrodes. SEM micrographs of the fracture surfaces of complete button cells revealed a dense, 150-µm thick electrolyte. The anode and cathode were observed to be only 2.5 and 5 µm thick, respectively, in the DKKK based cells, and in 30 and 40 µm, respectively, in the Praxair based cells (Figure 7).

During testing, the cells had open circuit voltage values of about 1.01 volts. Figure 8 shows the results of a current scan run at 800°C. The maximum current density achieved was only 25 mW/cm² at about 0.7 V. There are a few reasons why the cells did not perform well in the electrochemical tests. The thickness of the electrolyte should be decreased since it is one of the major sources of cell resistance. The reduction in the porosity of the cathode and anode due to sintering during testing also played a major roll in reducing cell performance. The densification of the electrodes during testing is clear from SEM images of the anode and cathode before and after electrochemical testing (Figure 9). This problem could be solved by adding pore-forming agents to the anode and cathode inks to increase the pore size, and therefore prevent further sintering during testing. Another possible reason for poor cell performance could be the formation of insulating secondary phases as a result of chemical reactions between both the LSFC and GDC cathode phases and between the LSFC cathode and the ScCeZrO₂ electrolyte. Research is in progress to study the possible interactions between the components of the cells.

CONCLUSIONS

Two commercial Sc₂O₃ – CeO₂ –ZrO₂ powders were compared for use as an electrolyte material for SOFCs. Button cells were manufactured via a two step sintering process; first the electrolyte tapes were fired, after which the electrode inks were screen printed onto the electrolyte and cofired. Complete button cells were examined using an SEM both before and after testing at 800°C for 2 hours. The first preliminary results showed poor cell performance, which is believed to be due to further sintering of the electrodes during testing, formation of a poorly conducting secondary phase, and thickness of the electrolyte. Further research is in progress for the manufacturing and testing of ScCeZrO₂ based cells.

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REFERENCES

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