CATHODE SUPPORTED THIN FILM SOFCs

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ABSTRACT

Co-firing of thin film ceramic electrolytes on highly porous cathode supports may allow significant cost reduction for both planar and tubular solid oxide fuel cells. Co-firing of La0.65Sr0.35MnO3 (LSM) supports with dense thin films of yttria stabilized zirconia (YSZ) and scandia stabilized zirconia (SSZ) was successfully demonstrated at 1250°C. Co-firing La0.9Sr0.1Ga0.9Mg0.1O3 (LSGM) electrolytes with the LSM cathode was also promising but did not yield dense films at 1250°C. Tri-layers consisting of a LSM cathode support, a dense YSZ electrolyte film, and a porous NiO-YSZ anode were also prepared, as well as La0.70Sr0.30CrO3 powders suitable for co-firing with the tri-layer cell.

INTRODUCTION

Many solid oxide fuel cell developers have focused their attention on cost reduction as the key strategy for successful commercialization of SOFC technology. One approach to reducing the stack and system cost is to reduce the operating temperature of the cells to 600-800°C where low cost alloys may be employed in the stack and the balance of plant; however, cell performance should not be compromised. Inexpensive materials and manufacturing are required for producing low cost cells. In this work, we focus on reducing the number of high temperature firing steps required for the production of solid oxide fuel cells. In this work, we create a fine-grained cathode microstructure, designed to improve electrochemical performance, by lowering the co-firing temperature to below 1300°C.

The motivation for this work is to lower the cell cost by reducing the total number of high temperature sintering steps, ideally to one. This approach is useful for anode or cathode supported cells. Using LSM as the support as opposed to Ni-YSZ can further reduce raw materials costs for thin-film ceramic SOFCs. LSM powders have estimated costs that are typically less than 1/3rd the cost of YSZ (1). Finally, the processing conditions needed for single step co-firing a complete tubular or planar cell that includes the cathode, electrolyte, anode, and interconnect are of interest for manufacturers of both planar and tubular cells.

The two key challenges to producing a high performance co-fired LSM supported cell are to minimize the reaction between the LSM and the electrolyte and to prevent excessive coarsening of the LSM structure so that a high triple phase boundary may be preserved in the cathode microstructure. Co-firing of the LSM cathode and YSZ electrolyte has been
previously demonstrated by several groups (2-5). Prior work in our group demonstrated a co-fired LSM supported device designed for oxygen separation. Cell performance was quite good ($\eta_{cell}$ 0.5 V at 1.55 A/cm$^2$) at 800°C (3) when the LSM-YSZ was sintered at 1400°C. In the present study, we have focused on reducing the firing temperature to 1200-1300°C to allow the use of more reactive electrodes, as well as introduce the possibility of co-firing La$_{0.7}$Sr$_{0.3}$CrO$_3$ interconnects with the cathode/electrolyte/anode structure to enable single step fabrication of planar and tubular SOFCs. In addition, we attempted to co-fire LSM/SSZ or LSM/LSGM bi-layers in order to demonstrate the use of higher conductivity electrolytes for cathode-supported cells. The techniques described can be used for co-firing cathode supported cells or anode supported cells for fuel cells or oxygen separation.

**EXPERIMENTAL**

La$_{0.65}$Sr$_{0.30}$MnO$_3$ (LSM) powder (d$_{50}$=1.3 µm, surface area ~4.71 m$^2$/g) was obtained from Praxair Specialty Ceramics (USA) and Timrex KS4 graphite pore former from Timcal Ltd (Switzerland). 50 g of LSM was attritor milled with Menhaden fish oil (3 wt%) using zirconia milling balls in IPA for 1 hr at 550 rpm. 17.5 g of the graphite pore former, 3wt% of polyvinyl butyral and dibutyl phthalate were added after milling was complete. The mixture was dried, ground with mortar and pestle, then sieved <150 µm. The resulting powders were then uniaxially pressed at 15 ksi in a stainless steel die. The resulting green disks were either used as is or prefired to 950°C for 4 hrs to remove the binder/graphite before thin film deposition.

8 mol% yttria stabilized zirconia (YSZ) powders were obtained from Tosoh Corporation (Japan). 9 mol% scandia stabilized zirconia (SSZ) powders were synthesized using the Pechini (4) process. La$_{0.9}$Sr$_{0.1}$Ga$_{0.9}$Mg$_{0.1}$O$_3$ (LSGM) and La$_{0.7}$Sr$_{0.3}$CrO$_3$ (LSCR) powders were produced by the glycine-nitrate (GN) (5) method. In the GN method, glycine was added to the solution in glycine/nitrate (G/N) ratios of 0.5 and combustion took place in a stainless steel beaker on a hot plate set to the highest level. The powders synthesized were used as-combusted or calcined (LSCR 800°C, SSZ 1000°C, LSGM 1400°C) in air for 1-4 hours and then attritor milled in isopropyl alcohol (IPA) using YSZ balls at the rotation speed of 550 rpm for 3-6 hrs. NiO-YSZ anode powder was also prepared by attritor milling for 1 hr at 550 rpm.

Electrodes and electrolyte layers were then applied with an aerosol spray gun. Colloidal deposition of ceramic films and electrodes by this method has been previously described (6). The ceramic powder is dispersed in IPA with the aid of a dispersant and applied to the porous support using an air brush. Sintering of the bi-layer or tri-layer structures was carried out at 1250°C for 4 hrs in air. In addition ~1 gram samples for dilatometry were uniaxially pressed in a $\frac{1}{2}$ in stainless steel die (5 ksi) and the percent linear change was measured as a function of temperature (Orton model 1600D dilatometer).

**RESULTS**

LSM porous supports with a density of 65-70% of the theoretical density were obtained by sintering in air at 1250°C for 4 hours. Dense films of YSZ and SSZ, shown in Figure
1 and 2, were successfully co-fired with the LSM support at 1250°C. LSGM films were also co-fired with LSM at 1250°C; however, as shown in Figure 3, through-porosity remained in the electrolyte film.

The current-potential characteristics of the LSM supported YSZ cell was then tested in air with Pt paste as the anode over a range of temperatures (Figure 4). For the LSM supported cells tested, no gas diffusion limitation was observed even at current densities above 2 A/cm² (not shown).

In these tests, the cathode was composed of LSM powder only. We believe that the cell performance will improve with the use of a mixed LSM-YSZ cathode and a Ni-YSZ anode. Given the encouraging results on cathode supported bilayers, co-firing of tri-layers consisting of porous LSM, dense YSZ, and porous NiO-YSZ was also attempted. The resulting tri-layer SOFC microstructure is shown in Figure 5 (fuel cell testing of the co-fired tri-layer cells is ongoing).
One of the challenges in co-firing tubular cells is matching the sintering of the lanthanum strontium chromite interconnect to the rest of the cell components. Sintering $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_3$ to $>$98% theoretical density at 1200-1250°C has been previously reported (7). The authors reported a drop in sintered density at 1300°C due to Cr loss. We attempted to fabricate $\text{La}_{0.7}\text{Sr}_{0.3}\text{CrO}_3$ (LSCr) interconnects by the co-firing route on the LSM supports. The sintering profile of the LSCr powder made by glycine nitrate combustion, as-combusted and calcined at 800°C for 1 hour, and the LSM powder is shown in Figure 6 below. Calcination did not improve the sintering of the LSCr powder, however the as-combusted material was reasonably well matched to the sintering profile of the LSM support and will be used for future work.

Figure 6. Sintering profiles of $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$+KS4 graphite, as-combusted $\text{La}_{0.7}\text{Sr}_{0.3}\text{CrO}_3$, and LSCr powder calcined at 800°C.
CONCLUSIONS

Reduction of the number of sintering steps required to produce single solid oxide fuel cells represents an important step towards lowering the total cost of SOFC stacks. We have demonstrated that co-firing of cathode-supported bi-layers and tri-layers is possible at 1250°C and have produced interconnect powders suitable for sintering with these materials. The approach described here may be used for cathode or anode supported cells, as well as planar or tubular geometries. The ultimate viability of this approach will depend on the electrochemical performance and long-term stability of SOFCs produced in this manner.

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