Short communication

Perovskite-related intergrowth cathode materials with thin YSZ electrolytes for intermediate temperature solid oxide fuel cells

Claudia Torres-Garibay[*], Desiderio Kovar

Materials Science and Engineering Program, The University of Texas at Austin, 1 University Station C2200, Austin, TX 78712, United States

ABSTRACT

The electrochemical performances of solid oxide fuel cells with thin yttria-stabilized zirconia (YSZ) electrolytes and YSZ/Ni anodes were studied with two intergrowth oxides cathodes ($Sr_{2.7}La_{0.3}Fe_{1.4}Co_{0.6}O_{7-\delta}$ and $LaSr_3Fe_{1.5}Co_{1.5}O_{10-\delta}$) and the results compared to a related perovskite cathode ($La_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$). It was found that cells produced with $LaSr_3Fe_{1.5}Co_{1.5}O_{10-\delta}$ exhibited peak power densities close to $0.75\,W\,cm^{-2}$, despite the relatively modest electrical conductivity of this compound. In contrast, cells produced with $Sr_{2.7}La_{0.3}Fe_{1.4}Co_{0.6}O_{7-\delta}$ and $La_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ cathodes both exhibited peak power densities of less than $0.4\,W\,cm^{-2}$. The greater performance for the cells produced with $LaSr_3Fe_{1.5}Co_{1.5}O_{10-\delta}$ may be attributed to a higher catalytic activity for this compound or to an improved adhesion of the cathode to the interlayer/electrolyte.

1. Introduction

Recently, there has been a drive to decrease the operating temperature of solid oxide fuel cells (SOFC) to intermediate temperatures (600–800 °C). Advantages of this temperature reduction are the reduction in internal stresses from thermal expansion mismatch between the cell components, and the ability to use less expensive metallic interconnects. However, there are significant challenges for both the electrolyte and cathode at these operating temperatures.

Yttria-stabilized zirconia (YSZ) is the most commonly used electrolyte material for high temperature SOFC due to its high ionic conductivity at elevated temperatures (~1000 °C). However, the resistivity of YSZ increases dramatically at lower temperatures resulting in high ohmic polarization. To compensate for the higher resistivity at intermediate temperatures, the electrolyte thickness for YSZ electrolytes can be reduced to minimize the ionic path length and thus, produce electrolytes with adequate ionic conductance.

(La,Sr)MnO₃ (LSM) perovskite has been used widely as a cathode material for SOFC operating at high temperatures, but the activation polarization for this material increases at temperatures below 900 °C [1]. To improve catalytic activity at intermediate tempera-tures, Mn has been substituted by Co resulting in a material with better performance at lower temperatures [2]. However, this material exhibits a high TEC [3] which is undesirable. A tradeoff between conductivity and TEC is achieved by partially substituting Co for Fe, resulting in (La,Sr)(Co,Fe)O₃ (LSCF) with a perovskite structure [3].

Perovskite-related intergrowth oxides from the Ruddlesden-Popper series $(La,Sr)_{n+1}(Fe,Co)_nO_{3n+1}$ with $n = 2$ [4] and $n = 3$ [5] are also good candidates for cathode materials for IT-SOFC due to their stability and their high oxygen ion conductivity. These materials are referred to as perovskite-related because a perovskite structure results when $n = \infty$. Recently, $Sr_{2.7}La_{0.3}Fe_{2-y}Co_yO_{7-\delta}$ ($n = 2$) [6] and $LaSr_3Fe_{3-y}Co_yO_{10-\delta}$ ($n = 3$) [7] have been explored as cathodes for SOFCs using thick, $La_{0.8}Sr_{0.2}Ga_{0.8}Mn_{0.2}O_{2.8}$ electrolytes. Although, it was shown that $Sr_{2.7}La_{0.3}Fe_{1.4}Co_{0.6}O_{7-\delta}$ (SLFCO7) and $LaSr_3Fe_{1.5}Co_{1.5}O_{10-\delta}$ (LSFCO10) exhibited good mixed electronic–ionic conductivity and structural stability, the overall cell performance was limited by the relatively poor conductance of the thick electrolyte. In this study we explore the use of the perovskite-related intergrowth oxides SLFCO7 and LSFCO10 as cathodes for IT-SOFC with thin YSZ electrolytes and results are compared to the related LSCF perovskite, $La_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$.

2. Experimental

Details of the manufacturing process have been published elsewhere [8], so only a brief summary is presented here. The electrolyte was prepared from 8 mol% YSZ (Tosoh) and the anode was prepared using a mixture of NiO (J.T. Baker) and 8 mol% YSZ (Tosoh) at a volume ratio of 54:46. The powders were dispersed by ball milling with

* Corresponding author. Present address: Materials Science and Engineering Department, University of Michigan, 2300 Hayward St., Ann Arbor, MI 48109, USA. Tel.: +1 734 223 0359; fax: +1 734 763 4788.
E-mail addresses: clautoga@alumni.utexas.net (C. Torres-Garibay), dkovar@mail.utexas.edu (D. Kovar).

Table 1
Electrolyte slurry for tape casting (adapted from Mukherjee et al. [11]).

Component	Function	ρ (g cm^{-3})	Wt%	Vol%
8-YSZ (Tosoh)	Ceramic powder	5.9	45.0	10.4
Ethyl alcohol	Solvent	0.79	22.2	38.5
Methyl ethyl ketone	Solvent	0.8	22.2	38.0
Phosphate ester	Dispersant	1.05	0.7	0.9
Polyvinyl butyral (Butvar B98)	Binder	1.1	4.2	5.2
Polyethylene glycol	Plasticizer	1.1	4.6	5.7
Benzyl butyl phthalate	Plasticizer	1.12	1.1	1.3

Table 2
Anode slurry for tape casting (adapted from Mistler and Twiname [12]).

Component	Function	ρ (g cm^{-3})	Wt%	Vol%
NiO (Baker)	Ceramic powder	6.67	35.4	9.6
8-YSZ (Tosoh)	Ceramic powder	5.9	26.6	8.2
Ethyl alcohol	Solvent	0.79	12.3	28.3
Toluene	Solvent	0.805	18.4	41.5
Phosphate ester	Dispersant	1.05	1.2	2.5
Polyvinyl butyral (Butvar B79)	Binder	1.083	3.1	5.2
Benzyl butyl phthalate	Plasticizer	1.12	3.1	5.0

a surfactant, a binder and plasticizer. Specific information about the compositions of the slurries, are given in Tables 1 and 2. The slurries were tape cast separately onto glass using a doctor blade with a gap of 100 μm for the electrolyte and 400 μm for the anode. Discs were punched from the dried tapes, stacked and hot laminated to produce the anode/electrolyte assemblies. The organics were pyrolyzed by slowly heating and the assemblies were subsequently co-fired for 2 h at 1400 °C.

Preliminary experiments showed that the cathode materials react with the YSZ electrolyte during processing. To prevent such reactions, for these studies, a thin $Ce_{0.9}Gd_{0.1}O_2$ (GDC) interlayer

was applied between the electrolyte and cathode. The GDC powders were prepared by solid-state reaction using the glycine-nitrate method [9]. A paste was prepared by mixing an equal weight fraction of GDC powder with an organic vehicle (W.C. Heraeus, V-006) and applied by screen printing onto the co-fired electrolyte/anode. The interlayer/anode/electrolyte was then fired for 2 h at 1300 °C.

LSCF perovskite oxide powders were synthesized by a co-precipitation method, employing La_2O_3 (Alfa Aesar), $SrCO_3$ (Alfa Aesar), $Co(CH_3COO)_2 \cdot H_2O$ (Spectrum), and $Fe(CH_3COO)_2$ (GFS Chemicals) as starting materials. Required amounts of the raw materials were dissolved in dilute nitric acid and a 10% (w/v) solution containing equal amounts of KOH and K_2CO_3 was added slowly until the pH rose above 11 to co-precipitate the metal ions as carbonates and hydroxides. The co-precipitate was filtered, washed with deionized water several times, dried overnight in an air-oven, calcined in air at 500 °C for 5 h, ground by hand, and fired in air for 24 h at 1200 °C. The products were then ball milled dry or ground in an agate mortar with ethanol to achieve the desired particle size distribution.

The intergrowth perovskite oxide powders were prepared by solid-state reaction in air. Stoichiometric amounts of La_2O_3, $SrCO_3$, Fe_2O_3 and Co_3O_4 were calcined in air for 12 h at 900 °C for SLFCO7 or 1000 °C for LSFCO10. After grinding in an agate mortar, the powders were fired for 24 h at 1300 °C with an intermediate grinding in an agate mortar after 12 h.

The cathode powders were mixed with an organic vehicle (W.C. Heraeus, V-006) at a weight proportion of 3:2 and applied onto the interlayer by screen printing in three passes. To determine the maximum allowable firing temperature for the cathodes, mixtures of powders of GDC and SLFCO7 and GDC and LSFCO10 were prepared and fired at temperatures of 1000–1300 °C and then examined using X-ray diffraction (XRD). The results indicate there are no reactions between GDC and SLFCO7 (Fig. 1a) or between GDC and
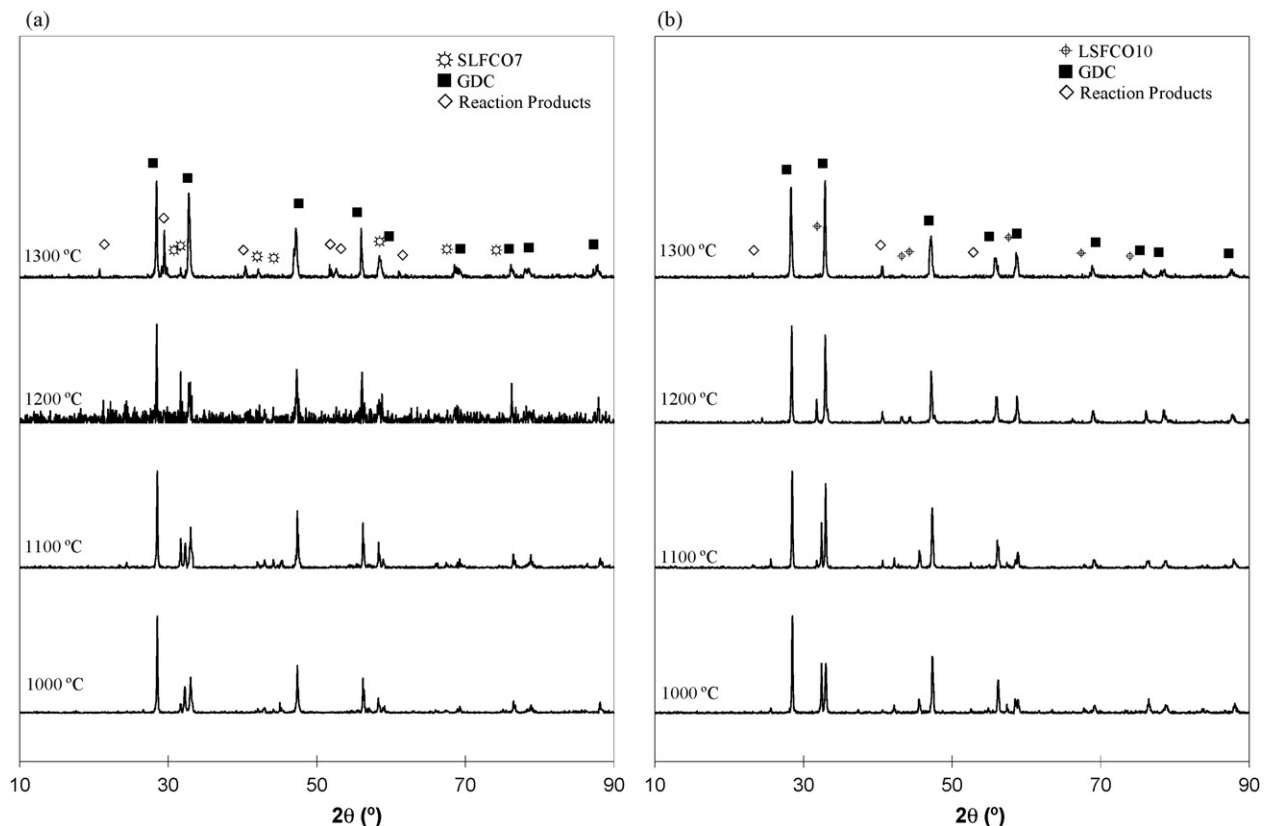
Fig. 1. X-ray diffraction spectra for powder mixtures of GDC and SLFCO7 (a) and LSFCO10 (b) after firing at 1000–1300 °C.
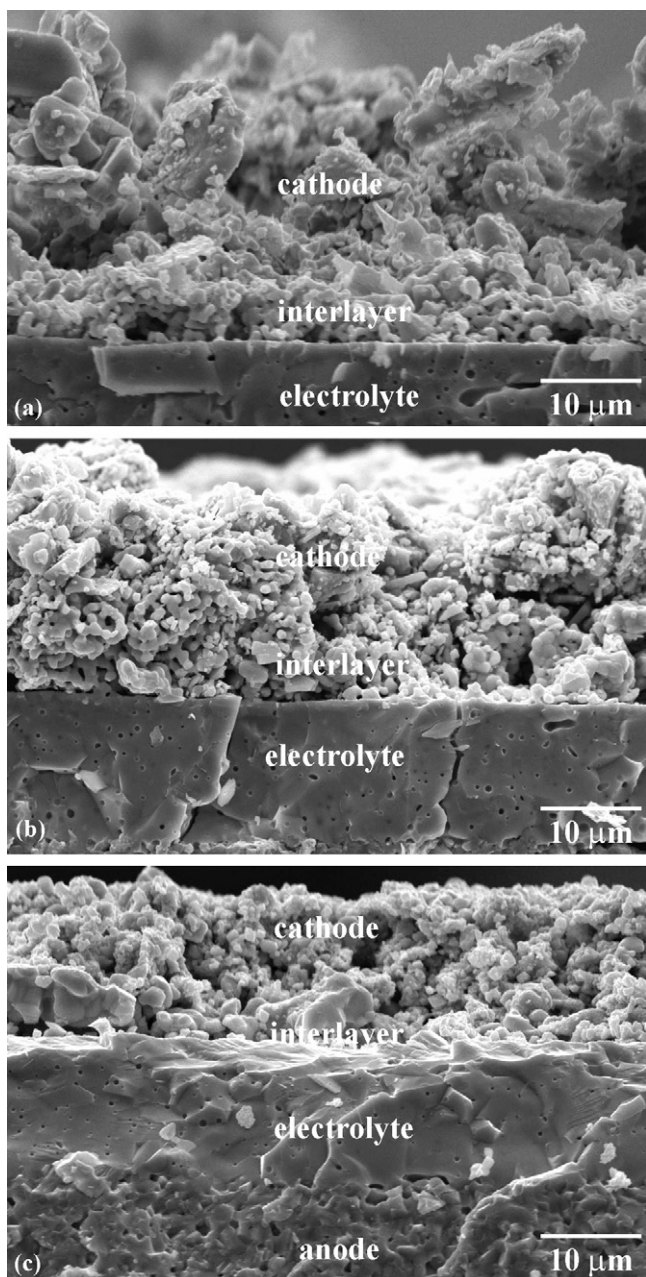
Fig. 2. Secondary electron micrographs of fracture surfaces of SOFC with (a) SLFCO7, (b) LSFCO10 cathodes, and (c) LSCF.
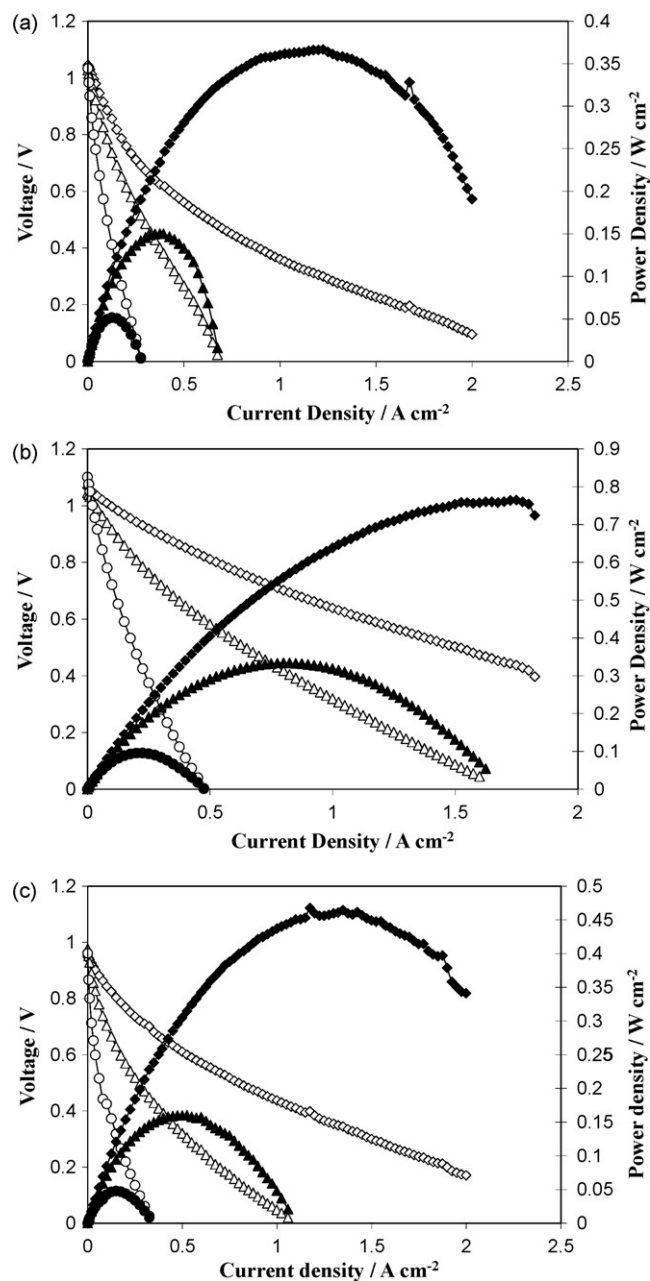

Fig. 3. I–V curves (open symbols) and power densities (closed symbols) of IT-SOFC with SLFCO7 (a), LSFCO10 (b), and LSCF (c) cathodes, for 800 °C (◊, ♦), 700 °C (○, ●), and 600 °C (△, ▲).

LSFCO10 (Fig. 1b) at temperatures of up to 1000 °C but that a reaction product is produced at higher temperatures. Thus, a firing temperature of 1000 °C for 2 h was used to sinter the cathodes.

Electrochemical performances were evaluated using single cells at temperatures of 600, 700, and 800 °C. Prior to the electrochemical evaluation of the cells, Pt current collectors of 0.25 cm^2 were attached to the electrodes using a small amount of Pt ink (W.C. Heraeus CL11-5100). During the tests, humidified H$_2$ was supplied to

the anode as fuel at a rate of 100 sccm and air was used as the oxidant. The NiO in the anode was reduced to Ni prior to beginning the test. I–V was measured in situ using an Arbin BT2000 battery fuel cell test station. At least two tests were performed for each material at each temperature; the results presented are an average of these tests.

3. Results and discussion

After firing, the fuel cells were flat with an electrolyte thickness of between 9 and 15 μm, and a total thickness of ~520 μm. Cross sections of representative, untested cells, obtained from scanning electron micrographs (SEM) of the fracture surfaces, are shown in Fig. 2. From these micrographs it is apparent that the electrolytes are dense containing only closed porosity and that there is good

Table 3
Maximum power densities (W cm^{-2}) obtained at operating temperatures of 600–800 °C, for IT-SOFC using $(La,Sr)_{n+1}(Fe,Co)_nO_{3n+1}$ cathodes.

Cathode	n	800 °C	700 °C	600 °C
SLFCO7	2	0.372	0.150	0.045
LSCFO10	3	0.739	0.338	0.101
LSCF	∞	0.378	0.159	0.045

adhesion between electrolytes, anodes, and GDC interlayers. The interlayers, determined using SEM in backscatter mode, are 5–7 μm thick and the thicknesses of the cathode layer are 15–17 μm. Both the anodes and cathodes exhibit sufficient porosity to ensure that gas flow can occur through the electrodes.

The firing temperatures for the cathode powders and the sintering temperatures for the cathodes were the same for all three cathode compositions. Nevertheless, it is possible that there are some microstructural differences between the sintered cathodes, although such variations are difficult to quantify. Another more clear difference between the SLFCO7 cathode and the LSCF and the LSFCO10 cathodes was that delamination, which is apparent between the SLFCO7 and the GDC interlayer, occurred readily during handling of the SLFCO7 cathode-containing cells but not for the LSCF and the LSFCO10 cathode-containing cells; delamination likely occurred during fracture of the cell rather than during cell preparation. This indicates that adhesion for this cathode was likely poorer than for the other cathode materials which did not exhibit such facile delamination.

The electrochemical performances of single cells are shown with SLFCO7 cathodes (Fig. 3a), LSFCO10 cathodes (Fig. 3b), and LSCF cathodes [8] (Fig. 3c) and the maximum power densities are listed in Table 3. The performances of the cells with SLFCO7 and LSCF cathodes are similar, although a comparison of the power density vs. current density curves (Fig. 3a vs. c) shows that the maximum power density is achieved at lower current densities with SLFCO7 cathodes. The maximum power density achieved with LSFCO10 cathode is nearly twice that for cells produced with SLFCO7 or LSCF and is comparable to that reported at 750 °C for cells using lanthanum ferrites in mixed cathodes [10].

The electrical conductivity of the cathode usually plays an important role in the performance of IT-SOFC. However, the maximum power densities for the cells tested in this study do not correlate directly with the electrical conductivity which indicates that other factors must play an important role in the performances of the cells. For the cathodes studied, at 800 °C, LSCF has the highest conductivity (333 S cm^{-1}) [3], followed by LSFCO10 (148 S cm^{-1}) [7] and then SLFCO7 (54 S cm^{-1}) [6]. The trend in conductivities is consistent with the fact that when $n = \infty$ (LSCF) the conductivity is isotropic, whereas for lower values of n, the electronic transport along the z-axis is lower than that along the x and y directions. This anisotropy in conductivities may explain the lower conductivities of polycrystalline SLFCO7 and LSFCO10 relative to the LSCF cathode material.

Examination of the I–V curves in Fig. 3 show that cells with the LSFCO10 cathode exhibit significantly lower activation polarization compared to cells with the SLFCO7 and LSCF cathodes. There are several possible reasons for the lower activation polarization for LSFCO10 including: (a) greater catalytic activity of this compound, (b) a larger number of reaction sites within the cathode, and (c) better adhesion between the cathode and the interlayer/electrolyte/anode assembly. The intrinsic catalytic activity is directly related to the chemistry of the cathode whereas the number of reaction sites and the adhesion are influenced by the microstructure. Since all the cathodes were fired at the same temperature, it is not likely that there were large differences in the number of reaction sites. This suggests that either LSFCO10 is more catalytically active than the other two compounds [4,5], or there are significant differences in adhesion between the cathodes and the interlayers. However, further work is needed to isolate possible microstructural effects, including differences in adhesion between the cathodes and the interlayers and possible cathode particle size effects, from the effects of catalytic activity.

4. Conclusions

Single cells of IT-SOFC were prepared with thin YSZ electrolytes $\sim$12 μm thick by tape casting and co-firing. The performance of these cells was investigated with perovskite-related intergrowth cathode materials $Sr_{2.7}La_{0.3}Fe_{1.4}Co_{0.6}O_{7-\delta}$ (SLFCO7) and $LaSr_3Fe_{1.5}Co_{1.5}O_{10-\delta}$ (LSFCO10) and compared to the related perovskite $La_{0.6}Sr_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ (LSCF). The use of a $Ce_{0.9}Gd_{0.1}O_2$ (GDC) interlayer was required to avoid undesirable reactions between the electrolyte and the cathode during cell fabrication. Single cells with the LSFCO10 perovskite-related cathodes showed the best performance despite having lower conductivity than LSCF. Further work is needed to determine whether the higher measured performance for LSFCO10 is a result of better catalytic activity for this compound or instead due to microstructural effects.

Acknowledgments

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