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Co-casting and co-sintering of porous MgO support plates with thin dense perovskite layers of $LaSrFeCoO_3$

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Abstract

A tape casting co-sintering route is described in which thin dense layers of $LaSrFeCoO_3$ (LSFC) have been formed on planar, porous MgO substrates 100–200 μm thick. SEM analysis of the sintered structure showed that it was possible to eliminate most of the residual porosity in the LSFC layer, but maintain a porosity between 25 and 45% in the MgO support layer. The LSFC layer did not reveal many cracks. The overall shrinkage of the co-sintered structure was about 25%. The LSFC layer topography was smooth and uniform with a metallic-like lustre. A good correlation was obtained between the observed microstructure and the gas permeability measurements made at room temperature.

Keywords: Calcination; Films; Membranes; Sintering; Tape casting

1. Introduction

Membrane reactors based on the use of mixed ionic–electronic conductors (MIEC) for the separation of oxygen from air are currently being developed for synthesis-gas production.[1–3] One particular approach uses a porous support of MgO on which is deposited a thin dense layer of MIEC material, such as lanthanum strontium iron cobalt oxide $LaSrFeCoO_3$ (LSFC).[4,5] In the present study, efforts have been focused on the fabrication of thin dense layers of LSFC of 5–10 μm on a much thicker support layer of magnesium oxide, 100–200 μm thick.

The preferred preparative route was co-tape casting. The two layers were co-cast in one production step using an aqueous based slurry. The green co-cast layer was then dried and co-sintered to form the ceramic membrane. Samples were made using MgO powder which had been pre-calcined at either 1000 or at 1200 °C.

After co-sintering, the membrane samples were tested for gas tightness using a permeability apparatus constructed "in-house". This was followed by SEM analysis for microstructural information. Open porosity and shrinkage rates were also determined.

2. Experimental

The cobaltite perovskite powder was supplied by EMPA (Swiss Federal Laboratories of Materials Testing) and manufactured according to a proprietary method. The exact composition used was $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ (LSFC). The powder was used in the "as received" state with no further calcinations, and had an average particle size of 1.5 μm.

The MgO powder was obtained from Fluka as a light grade type. This particular preparation had a very high surface area and was found to be quite reactive with water. In order to minimize water reactivity and to assist in the stability and rheology of the tape it was found necessary to pre-calcine the MgO powder before use. This was done at two temperatures: 1000 and 1200 °C, each for a duration of 4 h.

The MgO and LSFC powders were made into separate aqueous dispersions. Batches of 50 g powder were mixed with water and dispersant (Duramax D-3005 from Rohm & Haas) and then ball-milled overnight to produce the working dispersion. Optical microscopy

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was carried out to determine that all the agglomerates had been broken down.

The next step was to prepare slurries of the two dispersions for the tape casting process. This was done by taking 10 g quantities of the dispersed powder and mixing them with pre-determined amounts of acrylic binder (20–40% PVA). The amount of binder was chosen to give a flexible green tape after drying.

After degassing under vacuum, the slurries were ready for tape casting. This was done on a flat clean plate using a metal doctor blade held in position with a carriage made "in-house".

The tapes were left to dry overnight before cutting into disc shape samples of diameter 28 mm, a dimension suitable for the permeability apparatus. The samples were then sintered in a furnace (Lenton) at 1400 °C for 6 h.

The sintered samples were then tested for gas permeability in a specially constructed test rig. Essentially, the specimen was sandwiched between two glass flanges using silicone rubber gaskets. The pressurized side of the housing was then connected to an all metal system comprising a gas storage vessel (150 cm^{-3}), a pressure transducer (Wika Tronic), and a control valve to set the starting pressure. Nitrogen was used as the test gas, and supplied to the system at a pressure of 300 mbar. The pressure transducer was then connected to a PC for data acquisition.

Microstructural studies were then carried out using a SEM (Phillips XLF-30).

3. Results and discussion

A comparison was made between samples using the MgO powder calcined at 1000 and at 1200 °C, but otherwise using identical processing and sintering at 1400 °C. Some reference samples were made without the co-formed LSFC layer.

The results of the surface area measurements of the calcined MgO powder are given in Table 1.

The surface area of the 1000 °C-calcined sample was similar to the "as-received" sample, but the value for the 1200 °C-calcined sample was a factor of 10 lower.

The reaction of MgO with water derives from the basicity of the oxide, which forms $Mg(OH)_2$. This leads to instability of the aqueous dispersion causing agglomeration and eventual solidification over a period of several days. Calcination reduces the activity of the powder and so retards the hydration process.

Table 1
BET Multipoint surface area measurements obtained on MgO powder calcined at two different temperatures

Calcination temperature (°C)	Surface area $m^2 g^{-1}$
"as received"	41.02
1000	48.24
1200	4.36

Table 2 shows the % shrinkage of the sintered ceramics and the open porosity measurements obtained in water and propanol, for the two calcination temperatures investigated.

The SEM images of co-cast tapes derived from the 1000 °C calcined MgO powder are given in Figs. 1 and 2 while those of the 1200 °C-calcined powder are given in Figs. 3 and 4. Fig. 5 shows the room temperature permeability measurements taken on complementary samples.

The SEM cross-section images show, in both cases, the formation of a thin layer of LSFC approximately 5–10 μm in thickness on a porous layer of MgO. The morphology of the perovskite layer was fairly uniform, but some pin holes and cracks were apparent. This was particularly seen in the case of the 1200 °C-calcined MgO sample, but was less apparent in the case of the 1000 °C-calcined MgO sample.

Fig. 2 shows a close up view of the surface of the LSCF layer in which angular grains are formed. Some crystallographic planes are clearly visible, indicating that the material had experienced grain growth. Fig. 3 shows a cross-section of the MgO support layer which shows considerable porosity. Fig. 4 shows a close-up of the interface region between the LSFC layer and the MgO support layer. The MgO appeared to have

Table 2
Shrinkage and open porosity measurements of MgO-LSFC tape cast samples, sintered at 1400 °C for 6 h—method 1 used water uptake, method 2 used propanol uptake

Calcination temperature (°C)	% Shrinkage	% Porosity method 1	% Porosity method 2
1000	28	26.1	25.7
1200	22	41.5	42.5

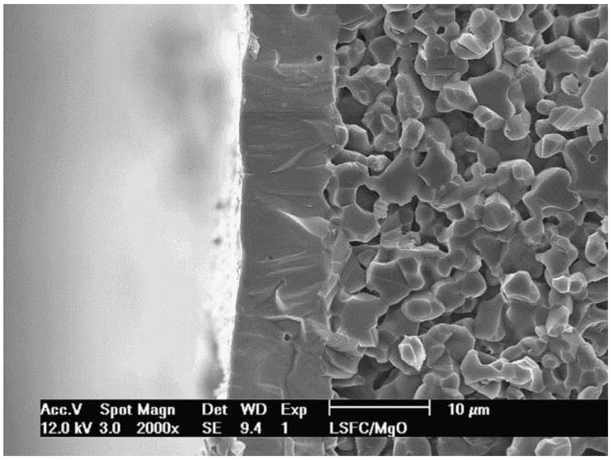

Fig. 1. SEM image (2000×) of a cross-section of a 1200 °C MgO–LSFC layer showing dense LSFC and porous MgO.

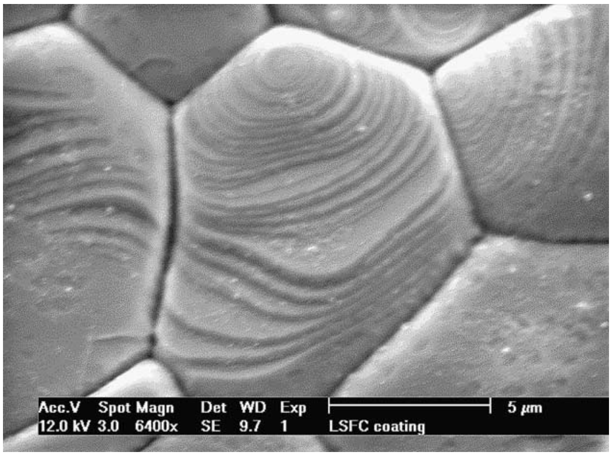

Fig. 2. SEM image (6400×) of the surface of a dense LSFC layer, showing angular grains, and crystallographic planes.

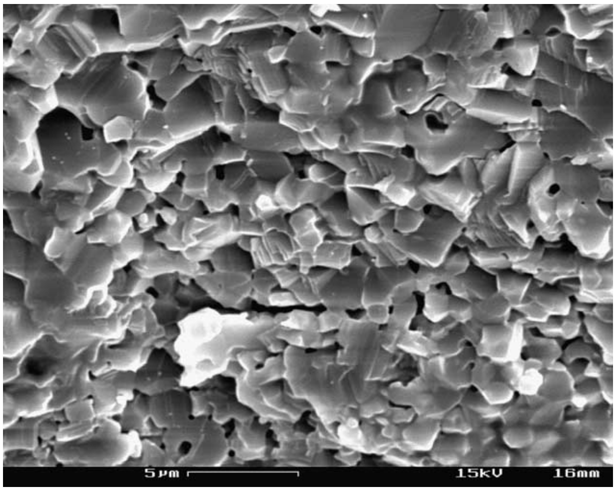

Fig. 3. SEM image (6000×) of a cross-section of a 1000 °C MgO–LSFC layer showing the porous MgO support.

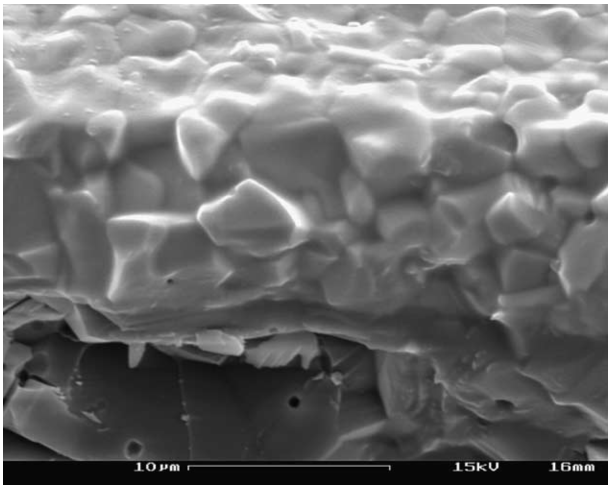

Fig. 4. SEM image (3000×) of a cross-section of a 1000 °C MgO–LSFC layer showing a dense LSFC layer on the MgO support. Closed pores are visible in the MgO grains.

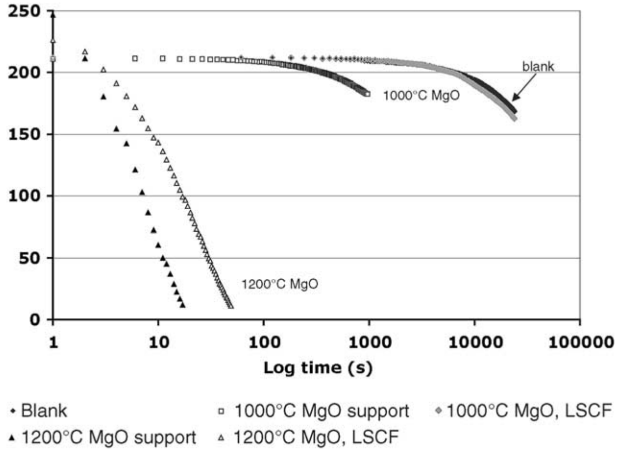

Fig. 5. Permeability measurements obtained on LSFC–MgO samples. Time is plotted as log elapsed seconds and the *y* axis is the output from the pressure gauge. The samples are grouped according to the MgO calcination temperature.

densified to some extent in this region as evidenced by the formation of closed pores. This was more apparent in the case of the 1000 °C-calcined MgO material than in the case of the 1200 °C-calcined material.

Fig. 5 shows the permeability results. The data is grouped according to the calcinations of the MgO powder. For the 1200 °C-calcined powder, the overall permeability is very high, both in the case of the uncoated MgO specimen, and in the case of the perovskite coated sample. The perovskite layer certainly reduced the permeation of nitrogen, but this specimen was not deemed to be sufficiently gas tight for practical use. On the other hand, the MgO powder calcined at 1000 °C showed excellent gas tightness. The sample containing the perovskite layer gave exactly the same response as the blank dense sample (YSZ) used to calibrate the test rig. A repeat measurement on the coated specimen also gave exactly the same gas tight response. A second sample from the same tape also confirmed gas tightness. The uncoated MgO sample calcined at 1000 °C showed high gas permeability relative to the complementary perovskite coated sample, but a much lower permeability than the uncoated MgO sample at 1200 °C. Clearly some densification of MgO had taken place, which was more apparent in the case of the 1000 °C-calcined powder. This correlates well with the SEM observations. A lower calcination temperature facilitates densification because smaller grains and higher adsorption of surface species leads to enhanced reactivity during the sintering process.

Further evidence of densification during sintering is apparent when considering both the open porosity measurements and the percentage shrinkage rates, as given in Table 2. The open porosity in the 1000 °C-calcined powder (26%) was much less than that of the

1200 °C-calcined powder (42%). Likewise the shrinkage of the 1000 °C-calcined powder (28%) was higher than the 1200 °C powder (22%).

4. Conclusion

The results of co-sintering LSFC with MgO powder calcined at two different temperatures (1000 and 1200 °C) showed that densification of the MgO substrate can exert a large influence on the permeation of gas through the membrane. This is partly due to a reduction in the open porosity of the bulk of the MgO substrate and partly due to the integrity and uniformity of the thin perovskite coating. There is some evidence that the MgO can further densify at the interface with the LSCF layer. The LSFC membranes made from the 1000 °C MgO powder were comparatively gas-tight at room temperature. Further work will determine the permeation rates of oxygen through the LSFC–MgO membranes at elevated temperatures.

Acknowledgements

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