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Ceramics International 35 (2009) 2493–2497

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Characterization of porous lanthanum strontium manganite (LSM) and development of yttria stabilized zirconia (YSZ) coating

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Received 27 June 2008; received in revised form 23 September 2008; accepted 12 November 2008
Available online 3 December 2008

Abstract

Cylindrical shapes of lanthanum strontium manganite (LSM) with varying amounts of pore former have been fabricated by the extrusion technique. Density of the sintered samples was found to decrease with the addition of pore former. Pore size distribution in a sintered sample with 37% porosity was within the range of 2–20 μm. Electrical conductivity of LSM samples with 20% and 32–37% porosity was found to be ~92 S/cm and ~80 S/cm, respectively. The thermal expansion coefficient of the LSM samples was found to be independent of porosity in the 20–37% porosity range. Sintered LSM tube was coated with YSZ by dip coating. Cross-sectional view of the coated sample showed formation of a dense layer of YSZ on the porous cathode structure.

Keywords: Fuel cell; Lanthanum strontium manganite; Prosity; Electrical conductivity; Extrusion

1. Introduction

Cathode of solid oxide fuel cell (SOFC) is subjected to oxidizing atmosphere. High temperature in combination with oxidizing atmosphere makes the selection of materials for cathode in SOFC very stringent. A few materials have been studied as prospective candidates for their use as cathode in SOFC [1,2]. Strontium doped lanthanum Manganite ($La_{1-x}Sr_xMnO_3$ or LSM) is found to be the most potential cathode material in stabilized zirconia electrolyte based solid oxide fuel cell [3–9]. Most preferred candidate material in this system is $La_{0.8}Sr_{0.15}MnO_3$ owing to its high electronic conductivity and physical and chemical compatibility with other components at operating temperature. Although LSM is a well characterized material, most of the studies conducted were on dense LSM samples, usually made by the conventional compaction method. In our earlier work [10], we have established a flow sheet for the synthesis of LSM powder by the co-precipitation method and cold compacted and slip cast materials were characterized. Subsequently, we have also demonstrated that a good chemical compatibility exists between in-house synthesized LSM and yttria stabilized zirconia powder [11]. In a recent publication, fabrication of a porous LSM tube by extrusion has been reported by Yamaguchi et al. [12]. However, no details could be found regarding the characterization of the developed material with respect to porosity, electrical conductivity and coefficient of thermal expansion. Therefore, it was considered worthwhile to develop porous LSM shapes by extrusion, to carry out their characterization, coating of an impervious layer of electrolyte on the porous tube and measure the open circuit voltage (OCV) of the developed single cell.

2. Experimental procedure

In-house synthesized phase pure lanthanum strontium manganite ($La_{0.85}Sr_{0.15}MnO_3$) powder [10] calcined at 1300 °C was used in the present study. The LSM powder, mixed with an aqueous solution of plasticizer (Polyethylene glycol or PEG), pore former (graphite) and binder (Polyvinyl alcohol or PVA) was extruded. The ratio of solid powder, water, plasticizer and binder was maintained at 70:20:7:3 and the amount of pore former was varied within 0–15 wt.% (0, 8, 10 and 15 wt.%). Dried extruded samples were sintered at 1400 °C for 3 h (heating rate of ~75 °C/h) with an intermediate soaking of 1 h at 800 °C. Phase purity of the sintered LSM (ground to powder form and annealed at 1000 °C) was investigated by X-

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doi:10.1016/j.ceramint.2008.11.012

ray diffraction. Bulk density and porosity of sintered specimens were determined by the water displacement method. Pore size distribution of the sample having maximum porosity was measured by mercury porosimetry (Model PASCAL 440, Thermoelectron Corporation, Italy). Microstructural features were investigated on the polished, thermally etched (at 1350 °C, 30 min) samples coated with a thin layer of silver with scanning electron microscope.

The electrical conductivity measurements were carried out in air in the temperature range of 200–1000 °C by the four probe technique. A double push rod dilatometer (Model TD5000S make MAC Science, Japan) was used to determine the coefficient of thermal expansion (CTE) of the sintered samples in air in the temperature range of 100–1000 °C.

A suspension of in-house make nano YSZ powder [13] in ethanol (containing 1 wt.% polyvinyl butryl as binder) was prepared by ultrasonicating the mixture for 30 min. The suspension was left overnight for settlement of agglomerated particles. The porous LSM tube was dipped manually in the stable suspension to apply coating by multiple dip coating. Development of coating at different stages was recorded at 500X by optical microscopy. The coated tube was sintered at 1400 °C. Coating features were analyzed by SEM fractography.

A slurry containing the fuel electrode (NiO–YSZ corresponding to 35 vol% of Ni–prepared in house) was applied on the electrolyte and was heat treated at 1300 °C. The single cell was tested for open circuit voltage using the ‘ProboStat’ system (Norwegian Electro Ceramics AS, Norway). Air was used as an oxidant, and hydrogen as fuel.

3. Results and discussion

3.1. Sintering and microstructure

The sintering behaviour of the extruded samples, i.e. bulk density (percentage theoretical density or %TD) and open porosity in presence of different amount of pore-former is shown in Fig. 1. A decrease in bulk density and increase in open porosity with increasing amount of pore former was observed. This is similar to the trend observed for slip cast sample [10]. LSM sintered at 1400 °C without pore former retained 20% open porosity. To increase the amount of porosity in the 1400 °C sintered product, pore former was added to the starting powder. Microstructure of the ~37% porous body is shown in Fig. 2. Pores are found to be uniformly distributed in the sample. The size of the pores were within the range of 2–20 μm, with maximum population density in the ~6–10 μm range. Pore size distribution in the same sample measured by mercury porosimetry appeared to be narrow and monomodal (within the range of 2–15 μm) with an average pore diameter ~8 μm (Fig. 3).

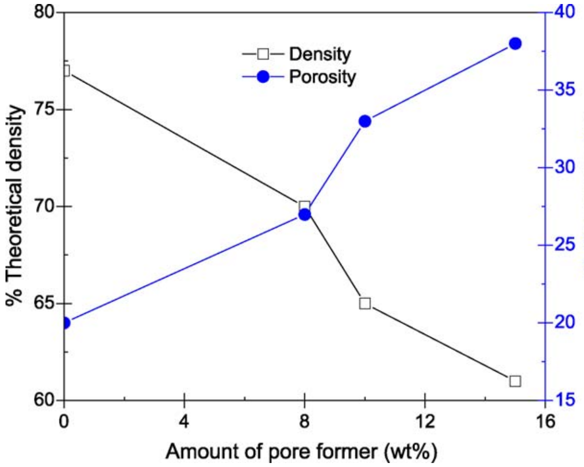

Fig. 1. Sintering behaviour of the extruded LSM sample with different amount of pore former (sintering at 1400 °C).

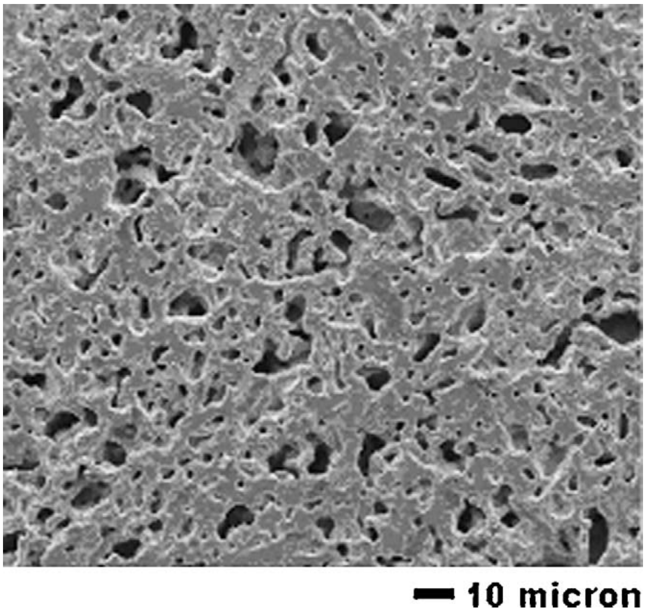

Fig. 2. SEM picture of thermally etched surface of 37% porous LSM sample.

3.2. Electrical conductivity

Plots of log(σT) vs. 1000/T (Fig. 4) for the samples with 0, 10 and 15 wt.% pore former show a linear behaviour with negative slope. The activation energy for conduction, E_a calculated from

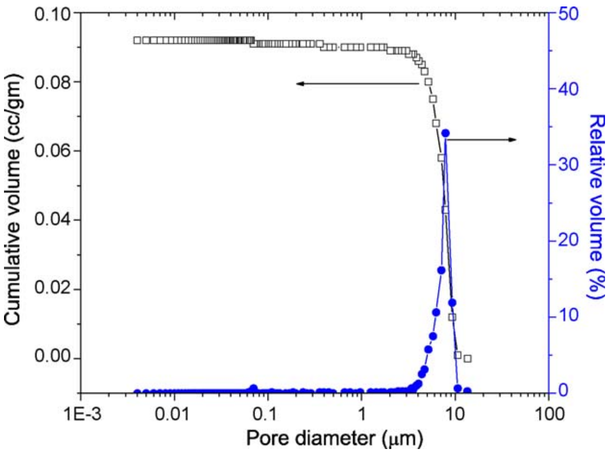

Fig. 3. Pore size distribution of sintered LSM with 37% porosity.

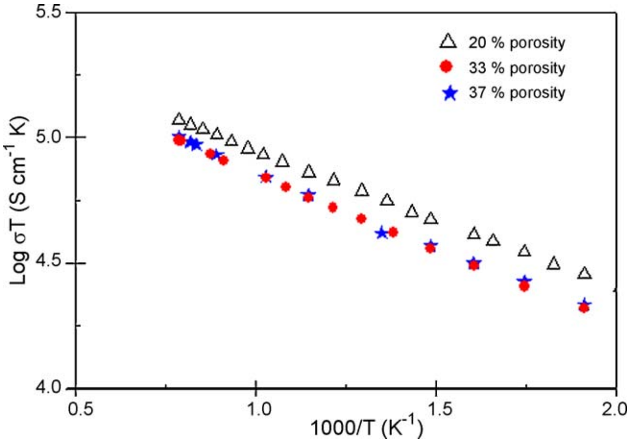

Fig. 4. Variation of $\log \sigma T$ with inverse of temperature (1000/T) for $La_{0.85}Sr_{0.15}MnO_3$ with varying porosity.

the slopes of these plots are found to be ~0.1 eV, which is in good agreement with reported value of activation energy for small polaron conduction in $La_{0.85}Sr_{0.15}MnO_3$ [14]. Conductivity σ at 1000 °C for LSM with 0, 10 and 15 wt.% pore former are 92, 77 and 79 S cm^{-1}, respectively. σ for slip cast and sintered sample with 40% porosity was 80 S cm^{-1} at 1000 °C [10]. σ was found to be higher in the sample where there was no pore-former present. This may be either due to the higher amount of porosity in the sample containing 10–15 wt.% of pore former or may be due to change in the structure of LSM. The latter may occur due to the reducing sintering atmosphere caused by burning of the pore former, which may affect the Mn^{3+}/Mn^{4+} ratio in the sample containing organic fugitive [15]. The activation energy for conduction was found to be independent of the amount of pore former. X-ray diffraction analysis of both the powders, obtained from a sintered sample containing 15 wt.% pore former (Fig. 5) and after calcinations at 1300 °C [10] confirmed presence of single phase distorted perovskite structure [11]. Conductivity of 79 S cm^{-1} at 1000 °C with 37% open porosity meets the conductivity requirement of SOFC cathode.

3.3. Thermal expansion

The thermal expansion (in %) and CTE as a function of temperature are shown in Fig. 6 for a LSM sample sintered in absence of pore former (20% porosity). Similar trend in thermal expansion behaviour was also observed for LSM with 10 and 15 wt.% pore former. For all these samples, the thermal expansion was found to increase monotonically over the entire temperature range of measurement. The CTE of LSM was found to be 10.9, 10.8 and 10.8 ppm °C^{-1} at 1000 °C for samples containing 0, 10 and 15 wt.% pore former, respectively. It shows that the variation of CTE within 20–40% porosity range is marginal. The CTE of porous LSM closely matches with CTE value of dense 8 mol% yttria stabilized zirconia (10.5 ppm °C^{-1}), which is the choice of electrolyte for high temperature solid oxide fuel cell [2].

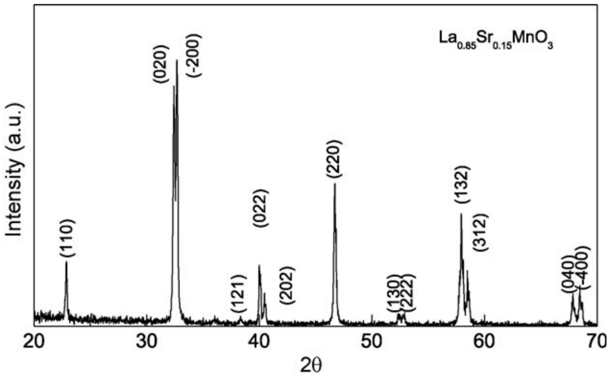

Fig. 5. Powder diffraction pattern of $La_{0.85}Sr_{0.15}MnO_3$ sintered at 1400 °C for 3 h.

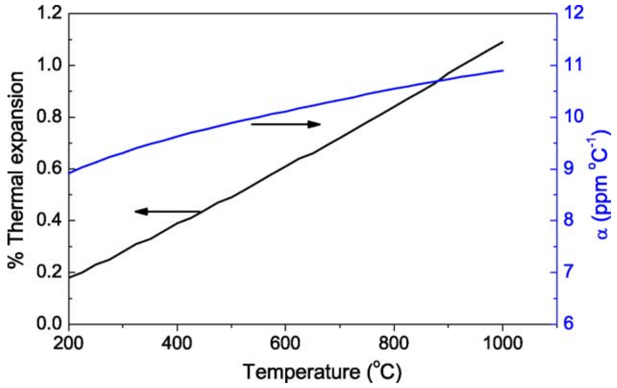

Fig. 6. Thermal expansion and coefficient of thermal expansion (α) of sintered $La_{0.85}Sr_{0.15}MnO_3$ with 20% porosity.

Fig. 7. Photograph of sintered LSM tube (contrast adjusted for clarity).

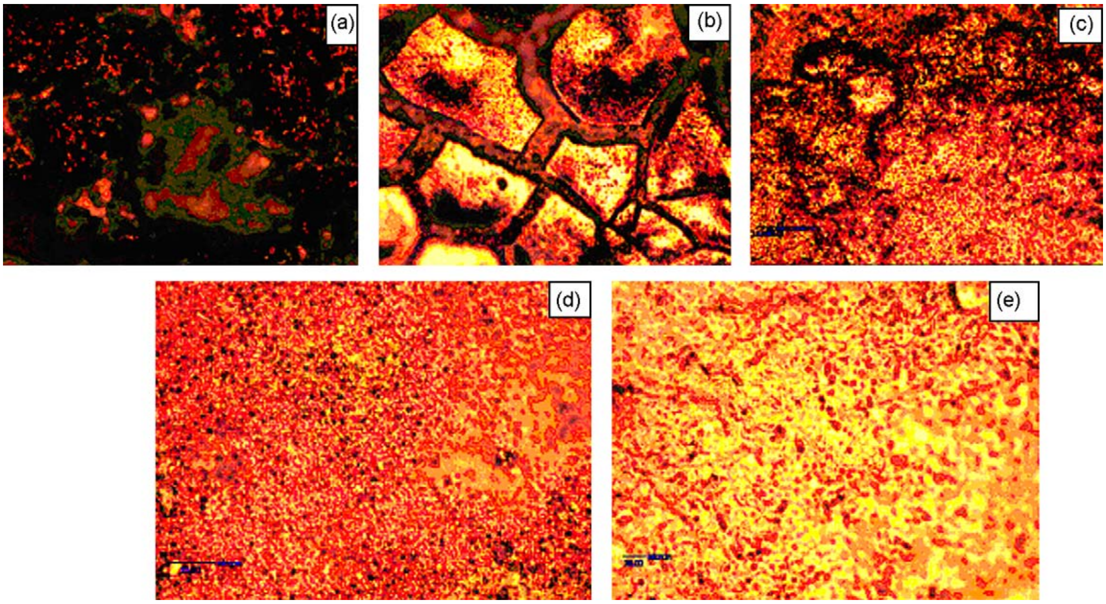

Fig. 8. Optical microscopic images of coated surface. (a) Bare surface of porous LSM tube, (b) cracked surface after first dip coating, (c), (d) and (e) are second, third and final dip coated (with YSZ electrolyte) surfaces, respectively.

3.4. *Coating microstructure*

Extruded cathode tubes prepared from LSM with 15 wt.% pore former and sintered at 1400 °C fulfilled the requirements of SOFC cathode in terms of porosity, electrical conductivity and coefficient of thermal expansion [2]. A 200 mm long (37–40% porous) LSM tube (sintered at 1400 °C) of 18 mm outer diameter (OD), 2 mm wall thickness is shown in Fig. 7. Smaller tubes (10 mm OD, 1.5 mm thickness and 30 mm in length) were used for carrying out the coating work. Multiple coating by dipping was applied for obtaining defect free dense layer. Surface features at different stages of coating are shown in Fig. 8. It is evident that defect left behind after each coating step was healed in the subsequent coating step. SEM fractograph of the cross-section of the YSZ coated LSM tube fired at 1400 °C is shown in Fig. 9. The thickness of the coating was about 30 μm. The OCV of single cell was found to be ~1 V at 850 °C. The near theoretical value of OCV indirectly indicates that the coating is impervious in nature. Further characterization is required to confirm the imperviousness of the coating.

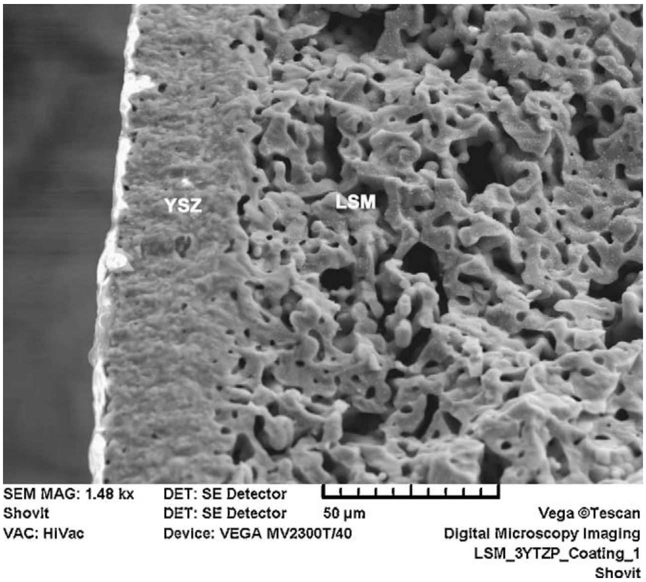

Fig. 9. Scanning electron micrograph of YSZ coated LSM tube (cross-sectional view).

4. Conclusions

Porous LSM tubes were fabricated after optimizing the amount of pore former. Sintered LSM with 15 wt.% pore former has been found to have 37% open porosity with uniformly distributed pores in the size range 2–15 μm. Electrical conductivity and coefficient of thermal expansion of this porous body at 1000 °C were 79 S cm^{-1} and 10.8 ppm $°\text{C}^{-1}$, respectively. Hence, the sintered tube fulfills most of the requirements for its use as a cathode in SOFC. The LSM tube was coated with YSZ by dip coating. The thickness of the coating was found to be about 30 μm and appeared to be quite dense.

Acknowledgements

The authors thank Shri B.P. Sharma, Director, Chemical Engineering Group, BARC and Energy Conversion Materials section, BARC for extending OCV measurement facility.

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