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ONE STEP PRODUCTION PROCESS FOR LARGE AREA SUPPORTING CATHODE

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ABSTRACT

Tape casting is a cheap and easily scalable shaping technique used to produce large-area, flat ceramic substrate for SOFC applications. To obtain elements with the desired porosity it is necessary adding a pore forming agent in the tape casting slurry. In this work, the possibility to obtain porous $La_{0.8}Sr_{0.2}MnO_3$-$Ce_{0.8}Gd_{0.2}O_2$ (LSM-GDC) supporting cathode without the use of pore formers was evaluated. The reactive sintering approach was therefore considered to exploit the porosity induced by the precursor decomposition during a single thermal treatment of calcining-debonding-sintering. Through this approach the $La_{0.8}Sr_{0.2}MnO_3$ phase was formed directly during the sintering step. This process allowed to obtain 10x10 cm^2 LSM-GDC tapes with values of mechanical strength, porosity and permeability suitable for fuel cells applications without pore former addition and in a single thermal step. To the author knowledge this is the first time that a large area supporting cathode has been produced by tape casting using the reactive sintering approach.

KEYWORDS

Fabbrication, Materials

INTRODUCTION

Solid oxide fuel cells (SOFCs) have attracted considerable research interest for their advantages as energy conversion devices [1-2].Among the possible cathode materials $La_{1-x}Sr_xMnO_{3-\delta}$ is commonly used for high temperature SOFC system with zirconia-based electrolyte. However these two materials can react forming an highly resistive $La_2Zr_2O_7$ phase that reduce the performances of the cell. To avoid this, a thin layer of gadolinia-doped ceria is generally interposed between these two layers [1-3]. Moreover to improve the electronic properties of the cathode and to better match the thermo-mechanical properties of the additional GDC layer a GDC phase can be add to LSM to form LSM-GDC cathode [3]. Cathode-supported SOFCs offer advantages over anode-supported ones in terms of structural stability. In fact, they do not suffer from volume contraction and expansion typical of the redox cycle of Ni-based supported cells [1].

The tape casting technique has been widely used to produce large-area, flat ceramic layers for SOFC applications [4]. This ceramic process is makes use of pore formers in the slurry to produce elements with engineered porosity [5]. This process however requires a careful modification of the slurry formulation to obtain homogeneous and flexible green tapes [5].

In this work, the possibility to obtain porous $La_{0.8}Sr_{0.2}MnO_3$-$Ce_{0.8}Gd_{0.2}O_2$ (LSM-GDC) supporting cathode without the use of pore formers was evaluated. The reactive sintering approach was therefore considered to exploit the porosity induced by the precursor decomposition during a single thermal treatment of calcining-debonding-sintering.

EXPERIMENTAL

Lanthanum, strontium and manganite precursor powder was produced using mixed oxide route in absolute ethanol starting from La_2O_3 (99,99%, Sigma-Aldrich), $SrCO_3$ (≥99,9%, Sigma-Aldrich) and $MnCO_3$ (≥99,9%, Sigma-Aldrich). The LSM precursor suspension was then dried at 60℃: part of this powder was calcined at 1100℃ for 2h to produce the $La_{0.8}Sr_{0.2}MnO_3$ pure phase, the other was used as-obtained in a tape casting slurry. The tape casting slurry was obtained by mixing the desired amount of LSM, $Ce_{0.8}Gd_{0.2}O_2$ powder (Fuel Cell Materials, Ohio, USA), azeotropic mixture of methyl ethyl ketone (MEK, Sigma-Aldrich) and ethanol (EtOH, Sigma-Aldrich), Butvar B98 (Monsanto Co.), polyethylene glycol (PEG 400, Fluka) and Santicizer 160 (Monsanto Co.).

The ratio of final LSM phase/GDC was fixed to 60/40 wt%. The final suspensions were deaerated under vacuum and casted on a moving Mylar carrier obtaining, after solvent evaporation, green tapes 800 ± 50 µm thick. The green tapes were cut and subsequently debinded and sintered in air at 1400℃ for 4 h. The debinding cycle was defined through thermo-gravimetric (TG) and differential scanning calorimetry (DSC) analyses (STA 449, Netzsch). The porosity of the sintered samples was evaluated by mercury intrusion technique (Pascal 140-240, Thermo Finnigan). The crystalline phase purity and the quantitative phase analysis of the sintered tape were assessed with a Bruker D-8 Advance X-ray diffractometer at room temperature using Cu anode as X-ray source, while its microstructure was investigated by scanning electron microscopy (SEM, Leica Cambridge Stereoscan 360). The permeability test were performed in an in-house testing rig using N_2 as gas and applying the Darcy's Law. The flexural tests were done on Zwick/Roell Z050.

RESULTS AND DISCUSSION

To assess the temperature needed to obtain a pure LSM phase the powder was calcined at temperatures between 1000 and 1100℃ for 2h and then analyzed through XRD. The thermal treatment at 1100℃ for 2h allows to obtain a pure perovskitic phase. Different tape casting slurries were formulated with this powder to obtain a flexible tape without defects. The debinding cycle was defined through TG analysis that shows a weight loss of 29% between 200℃ and 900℃ due to the precursors decomposition. Debinded tapes were then sintered at 1400℃ for 4h to obtain a large-area (10x10 cm) supporting cathodes (LSM-GDC 1).

SEM micrograph of the fracture surface of the sintered tape (Fig. 1a) shows a microstructure with low level of porosity, not suitable for SOFC applications; this result was confirmed by the porosimetric data that indicated a total porosity of 31% with an average pore diameter of 0.72 µm. To increase the level of porosity is a common practice to introduce a pore former (for example carbon black, rice starch or potato starch) in the suspension. This introduction requires a modification of the tape casting slurry formulation to obtain a crack-free tape [6] and a remarkable expenditure of time and materials. On the other hand in this case the high weight loss due to the precursor decomposition (29%) could be used to produce open porosity in the final tape. For this reason a new tape was produced (LSM-GDC 2) using the mixture of precursors instead of the pure phase-LSM powders and retaining the same formulation used for LSM-GDC 1.

TG analysis of this sample shows as the total weight loss of the LSM-GDC 2 tape is higher than the one of the previous formulation and is equal to 38%. This is consistent with the use of a non-calcined powder.

Debinded tapes were sintered at 1400℃ for 4h to obtain large-area (10x10 cm) supports (Fig. 2). XRD analysis of the sintered tape shows the presence of typical GDC fluoritic phase and pure LSM perovskitic phase without any additional phase. The phase ratio of the system (LSM-GDC 60/40wt%) was confirmed by Rietveld analyses. SEM micrograph of the fracture surface of the sintered tape (Fig. 1b) shows a microstructure with a good level of homogeneous porosity. The porosimetric data indicated a value of total open porosity equal to 45.1% and an average pore diameter of 1.23 µm.

The use of the precursors powder instead of an already formed phase allowed to increase both the value of total porosity and the average pore diameter without the use of pore former and with no particular modification of the tape casting slurry. This result is due to the precursors decomposition during a single thermal treatment of calcining-debonding-sintering. The LSM-GDC 2 electrode shows values of gas permeability and mechanical strength suitable for SOFC applications.

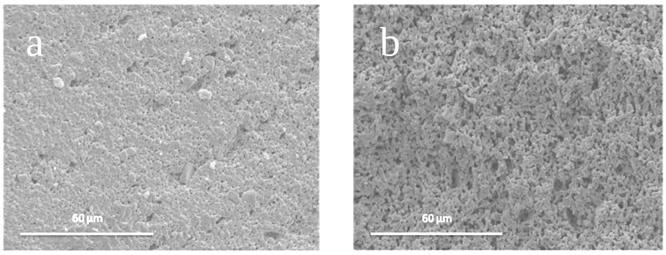

Fig. 1 SEM micrograph of the fracture surface of LSM-GDC 1 (a) and LSM-GDC (b) sintered tape.

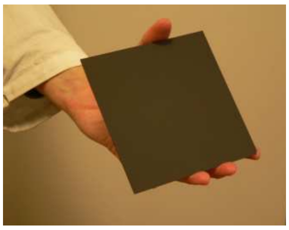

Fig. 2 Large-area (10x10 cm) sintered LSM-GDC 2.

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