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Alternative production route for supporting $La_{0.8}Sr_{0.2}MnO_{3-\delta}$-$Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (LSM-GDC)

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ABSTRACT

Tape casting is a widely used ceramic process that generally makes use of pore former agents to produce elements with engineered porosity for SOFC applications. In this work, porous $La_{0.8}Sr_{0.2}MnO_{3-\delta}$-$Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (LSM-GDC) supporting cathode of suitable porosity was produced using the reactive sintering approach without using of pore forming agent. The reactive sintering approach was considered in order to exploit the porosity induced by the precursor decomposition during a single thermal treatment of calcining-debonding-sintering. A stable tape casting slurry of lanthanum, strontium and manganite precursors and GDC powder was used in order to obtain large-area, crack-free green tapes. This process allowed to obtain 10 × 10 cm^2 LSM-GDC sintered tapes of thickness 600 μm with values of porosity and mechanical strength suitable for fuel cells applications, starting from the precursor mixture without the addition of pore former and avoiding any calcination step. Preliminary results show that the same conditions can be used to produce a LSM-GDC/GDC half-cell by co-firing this tape with on the top a screen-printed GDC layer. To the author knowledge this is the first time that the reactive sintering approach has been used to produce a large-area supporting cathode suitable for SOFC applications.

1. Introduction

Solid oxide fuel cells (SOFCs) and Solid Oxide Electrolyzer Cells (SOEC) have attracted considerable research interest for their many advantages as green energy conversion devices [1–4] and for the economical production of hydrogen [5–7] respectively. $La_{1-x}Sr_xMnO_{3-\delta}$-based materials are commonly used for devices that make use of zirconia as electrolyte. The two materials however can react forming an highly resistive $La_2Zr_2O_7$ phase that is detrimental for the electrochemical performances. For this reason, a layer of gadolinia-doped ceria (GDC) is commonly interposed between the two layers [1,8]. In this configuration, a mixture of LSM-GDC can be used to better match the thermo-mechanical properties of the additional GDC layer and to improve the electronic and catalytic properties of the electrode [1,8–10]. In SOFC mode, cathode-supported cells offer advantages over the anode-supported ones in terms of structural stability [11–14] as they do not suffer from volume contraction and expansion induced by the redox cycle of Ni-based supported cells [1]. In addition, because no vapor is formed at the cathode, the size of its pores can be smaller than the ones of a supporting anode, and therefore it can be thinner than the anode retaining the same mechanical strength [1].

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Tape casting is the most used technique for the production of ceramic layers with thickness in the range of 0.05–1.5 cm [15,16]. This technique is commonly devoted to the production of dense materials [17] but in recent years it has been widely employed also for the production of porous ceramic substrates for piezoelectrics [18–20], air separations [21,22], sensors [23,24] and SOFC applications [26,26]. This ceramic process is cheap and easily scalable and, in order to produce elements with engineered porosity, generally makes use of pore formers [18,27]. The addition of these kinds of materials in the tape casting slurry allows to finely tune the porosity in the final support by the direct control of the pore size distribution and pores amount in the sintered body. This process however requires a careful modification of the slurry formulation to obtain homogeneous and flexible green tapes [18,25,27]. For this reason many studies reported in literature [21,28,29] are focused on obtaining ceramic layers without the addition of pore forming agents. Studart et al. [29] report that the most straightforward processing route for the preparation of porous ceramics is the partial sintering of the shaped element. In this process the degree of porosity is in fact controlled by the degree of sintering, which, in turn, is controlled by temperature and dwelling time. This way however it cannot be used as a consequence of the high temperature needed to densify the GDC electrolyte for SOFC supporting electrode. Electrode and electrolyte bilayer for SOFC application are in fact generally co-sintered to obtain an electrode-supported half-cell. In order to obtain a dense GDC electrolyte membrane the sintering temperatures necessary are generally above 1300 °C. These temperatures dramatically reduce the porosity of the supporting electrodes as reported by Sanson et al. [25], Fontaine et al. [21] and Nie et al. [26] below the value of 40% necessary to allows the flow of the gases to and from the electrolytic membrane. This kind of engineered porosity is generally obtained only with the addition of pore formers. For SOFC application only few cases of tape casted SOFC electrodes has been produced without using pore formers [28,30]. These studies are restricted to Ni-based anodes where the porosity is induced by the NiO reduction. This effect cannot obviously be exploited for tape cast cathode for which the use of pore forming agents it is therefore necessary.

In this work, the possibility of obtaining $La_{0.8}Sr_{0.2}MnO_{3-\delta}$-$Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (LSM-GDC) supporting cathode with the SOFC suitable porosity without the use of pore formers using the reactive sintering approach was considered. The desired porosity was reached exploiting the precursors decomposition so that a suitable large-area supporting cathode was obtained in a single thermal treatment of calcining-debonding-sintering. Preliminary results showed that this approach can be used to produce a cathode-supported half-cell by co-firing the green tape with on top a screen-printed GDC electrolytic layer.

2. Experimental

Lanthanum, strontium and manganite precursor powder was produced in absolute ethanol (Aldrich) using the mixed oxide route starting from La_2O_3 (99,99%, Sigma–Aldrich), $SrCO_3$ (≥99,9%, Sigma–Aldrich) and $MnCO_3$ (≥99,9%, Sigma–Aldrich). The precursor suspension was dried in static air at 60 °C.

Half of this powder was calcined at 1100 °C for 2 h to produce pure $La_{0.8}Sr_{0.2}MnO_3$ whereas the other half was kept as dried mixture of precursors. Two tape casting formulations were prepared using these powders: the LSM mixed precursor (raw material-RM) and the $La_{0.8}Sr_{0.2}MnO_3$ pure phase (pure phase-PP). The stability of the two slurries was optimized considering different deflocculants: phosphoric ester (Fluka), 4-idroxy-benzoic acid (Sigma–Aldrich), 4-aminobenzoic acid (Sigma–Aldrich), furoic acid (Sigma–Aldrich), polyvinylpyrrolidone (Sigma–Aldrich), polivynylbutirral (B98, Monsanto Co., St Louis, MO, USA), stearic acid (Sigma–Aldrich). The sedimentation tests were performed on 5.0 vol% suspensions of the powder in the azeotropic mixture of ethyl alcohol and methyl ethyl ketone used as solvent for the tape casting slurry, and were carried out for 98 h in graduated cylinder. The concentration of each deflocculant was fixed at 1.2 wt% respect to the powder. The height of the sediment in each cylinder was measured as a percentage of the total solution height and used to define the most effective dispersant.

The formulations were prepared by mixing the desired amount of LSM, $Ce_{0.8}Gd_{0.2}O_2$ powder (Fuel Cell Materials, Ohio, USA) with the azeotropic mixture of methyl ethyl ketone (MEK, Sigma–Aldrich) and ethanol (EtOH, Sigma–Aldrich) as solvent, and Butvar B98 (Monsanto Co., St Louis, MO, USA) acting both as deflocculant and binder. The ratio of final LSM phase/GDC was kept at 60/40 wt%. Polyethylene glycol (PEG 400, Fluka) and Santicizer 160 (S160, Monsanto Co., St Louis, MO, USA) were used as plasticizers in 1:1 weight ratio among them. In the first stage solvent and deflocculant were mixed with LSM precursor powder by ball milling in polyethylene jar for 2 h to ensure good dispersion. After this time, GDC powder was added to the suspension. The binder was added after 24 h of ball milling whereas the plasticizers were added in a third step and milled for 24 h. The final suspensions were deaerated under vacuum and cast on a moving Mylar carrier ($v = 6$ mm/s) obtaining, after solvent evaporation, green tapes 800 ± 50 μm thick.

The green tapes were cut to obtain after sintering, cathodes of 10 × 10 cm^2 and then thermally treated in air at 1400 °C for 4 h. The LSM-GDC/GDC half-cell was produced screen printing a butyl carbitol acetate (Sigma–Aldrich) based ink of GDC (FCM, Lewis Center, Ohio, USA) on the surface of the LSM-GDC green tape and co-firing the entire structure at 1400 °C for 4 h.

The debinding cycle was defined through thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses carried out at 10 °C/min heating rate in a simultaneous thermal analyser (STA 449, Netzsch, Selb/Bavaria, Germany). The porosity of the sintered samples was evaluated by mercury intrusion technique (Pascal 140-240, Thermo Finnigan). The powder was characterized by X-ray diffraction (D8 ADVANCE, LynkEye detector-Bruker AXS, Germany) using CuKα radiation in the 10–80° 2θ range, scan rate of 0.02° (2θ), and 185 s equivalent per step. The quantitative phase analysis was performed using GSAS-EXPGUI software following RIR (Reference Intensity Ratio) and Rietveld refinement techniques [31,32].

The starting structural models were taken from Nagabushana et al. [33] for $La_{0.8}$ $Sr_{0.2}$ MnO_3 and from Brauer et al for