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Preparation and properties of thin $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ perovskitic membranes supported on tailored ceramic substrates

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Abstract

Mixed conducting $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSFC) perovskites are promising materials for oxygen separation membranes at high temperatures. Gastight 10–20 μm-thick perovskite layers were produced by vacuum slip-casting and screen printing on different porous substrates, i.e. $Ce_{0.8}Gd_{0.2}O_{1.9}$ (CGO), LSFC and composites of both. Some of the substrates are doped with cobalt for enhancing the mechanical stability and the shrinkage rate of the substrate. The manufacturing of the substrates and the different perovskitic asymmetric membranes are described in detail. The microstructure, the chemical compatibility between substrate and membrane, and the stability of the sintered layers were analyzed by scanning electron microscopy (SEM, EDX), SIMS and XRD at room temperature. Also the shrinking rates, surface smoothness, porosity and air permeance of the different substrate compositions are characterized. SEM analysis of the sintered top-layers showed a thickness of 10–20 μm, only closed porosity after sintering at 1200 °C and an He-leak rate in the range between 10^{-4} to 10^{-6} mbar l s^{-1} cm^{-2}. The thermal expansion coefficient and electrical conductivity of the membrane materials and the substrates are measured between 30 and 800 °C and oxygen flux measurements were carried out in the range 750–900 °C.

Keywords: Asymmetric membrane; LSFC; Oxygen separation; Perovskite; Mixed conducting membrane

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1. Introduction

The production of pure oxygen at high temperature through ceramic membranes constitutes a current challenge and would allow the introduction of more efficient and environmental-friendly power generation processes. Indeed, reliable O_2 separation would allow the operation of *Oxyfuel* power plants, which burn the fuel directly with nearly pure oxygen, obtaining in turn a flue gas uniquely composed of wet CO_2, which can be readily sequestered and liquefied. Moreover, different chemical processes would benefit by incremental improvements in ceramic O_2-permeable membrane technology, making possible the controlled oxygen addition through a catalytic surface and hence to increase the process selectivity but also allowing the process intensification by reducing the presence of large amounts of inert gases (N_2) in the converted stream. Examples of the selective catalytic conversion of chemicals mediated the use of perovskitic membranes have been recently reported for ammonia oxidation [1] into NO in the nitric acid industry and also for the selective oxidation of alkanes [2].

Mixed electronic–ionic conducting perovskites and related structures [3] are serious candidates for high temperature O_2-permeable membranes. Intensive research has been devoted in the last decade to the preparation and characterization of ferrite, cobaltite and nickelate-based membranes [4–7]. Nevertheless, few reports can be found with respect to the preparation of crack-free thin-films (thickness lower than 25 μm) for tubular or planar geometries whereas different groups have exhaustively studied the use of bulk perovskite hollow fibers [8,9] and monolith structures [10]. Even more interesting is the potential use of metallic substrates coated with thin perovskite films applied for example by plasma spraying [11], due to ease for module construction, sealing and suited mechanical properties.

The convenience of reducing significantly the thickness of the gastight layer is obvious due to its proportionality to the flux

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resistance up to a “characteristic thickness” in which the oxygen transport is not further governed by the bulk diffusion but by the surface exchange processes, involving different coupled elemental steps [12,13]: O_2 adsorption, dissociation and reduction. Consequently, the improvement of the permeation flux in the surface-controlled regime involves the increase of the surface area available of exchange processes as well as increasing the catalytic properties of the membrane top-layer. The magnitude of this *characteristic* thickness depends on the material and operating conditions. A rough value for $SrFeO_3$-based membranes is around 100 µm [12] and these ceramic thin-layers must be necessarily deposited on porous substrates. At this point, the problem of the selection of an appropriate porous substrate material and fabrication method arises, since many requirements are to be fulfilled such as (i) chemical compatibility, (ii) thermal expansion match, (iii) shrinkage behavior for obtaining a gastight top-coating, (iv) adjusted porosity for gas diffusion and surface area for oxygen exchange, (v) reliable upper surface for quality coating and (vi) mechanical properties. In this work we face this problem by studying and improving systematically the substrate properties to match the requirements for obtaining a crack- and pinhole-free $La_{0.58}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ top-layer. The variables we chose to move for the substrate improvement were (i) composition, by using different mixtures of $La_{0.58}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (LSFC) and $Ce_{0.8}Gd_{0.2}O_{1.9}$ (CGO), (ii) the use of sintering additives and (iii) the molding conditions (warm pressing), i.e. green density. The structural, textural, mechanical and electrical properties of the different substrates and coatings as well as the permeation properties of a supported thin-film are characterized. The particular CGO composition was selected due to its maximal ionic conductivity for all doped ceria, whilst LSFC stoichiometry due to the high ionic conductivity, the stability under operation conditions and the high electrocatalytic activity reported as SOFC cathode [14].

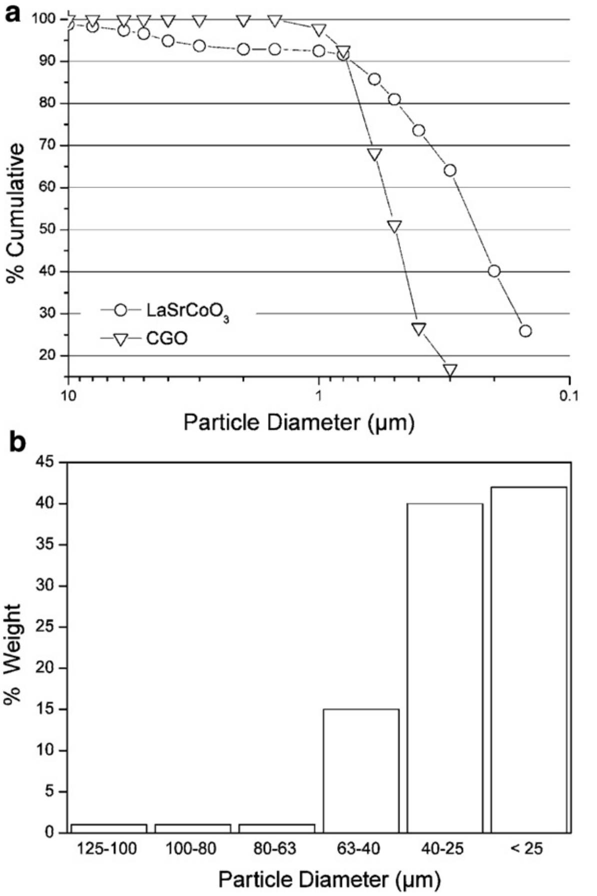

Fig. 1. Particle size distribution of (a) the ball-milled $LaSrCoO_3$ and CGO powders prior coating with the resin determined by centrifugation and (b) of the coat-mix granulate CM-4 determined by wet sieving.

2. Materials preparation and experimental methods

2.1. Substrates preparation

$La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (y = 0–0.8) perovskites were prepared by spray drying of the nitrate solutions containing all ingredients for each composition, and finally fired at 900 °C for 5 h. The calcined powders were examined by X-ray diffraction (XRD) to ensure phase purity and by ICP-AES to determine the exact composition. $Ce_{0.8}Gd_{0.2}O_{1.9}$ (CGO) was purchased from Treibacher (Austria). All the powders were preconditioned by ball-milling in ethanol in order to achieve an average particle size (d_{50}) of 0.2–0.3 µm. Fig. 1 presents two typical particle size distributions after milling. The manufacturing of the substrates of $7 \times 7 \times 0.2$ cm^3 by warm pressing (120 °C and 1 MPa) was performed using a special coat-mix® powder [15,16], where the surfaces of the corresponding ceramic grains are coated with a phenol formaldehyde resin (Bakelite®PF0790, Hexion). At first, the resin will be dissolved in ethanol. After this, the powder is dispersed in the binder solution. Acidic water (acetic acid 0.1 M) will then be added dropwise to the suspension, and the binder precipitates. The powder surface is coated with the binder and agglomerates are formed. The final binder content was around 20 wt.%. This powder consists of big porous agglomerates (d_{50} ~25 µm, see Fig. 1b) and therefore, the pressed substrates exhibit a high porosity and large pores after debinding, which ensures a fast gas exchange in high temperature asymmetric membranes and fuel cells. Another remarkable benefit of the use of a resin-coated powder is the relatively high mechanical strength properties of the as-molded substrate after resin cure even for geometries of 30×30 cm^2. The substrates were thermally treated in air for removing the binder and obtaining sufficient mechanical strength and porosity for handling and coating. The pre-sintering temperature of the substrates was 1100 °C with a constant dwell time of 3 h and the density was calculated by using the measured size and weight of the substrates. The optimized pre-sintering temperature program is outlined in Fig. 2a, being the final temperature 1100 °C and the dwell time 3 h. Table 1 lists the different substrate compositions prepared by mixing the corresponding amounts of CGO, the perovskite and sintering additive (Co_3O_4 produced by decomposition of cobalt nitrate) before resin coating. For improving the sintering behavior of the CGO-containing substrates, two options were considered: (i) impregnation of the CGO particles with a