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Development and characterisation of dense lanthanum-based perovskite oxygen-separation capillary membranes for high-temperature applications

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ABSTRACT

This research showcases the successful optimisation of the membrane fabrication process for a selection of lanthanum-based perovskite powders. A comparison is drawn between membranes made of LSCF and three of its cobalt-free analogues. Cobalt-free membranes have not been the subject of academic research to the same degree as LSCF and there have not been any reports of them being made into hollow fibre (capillaries). The present study examines how membrane performance is affected by the properties of the starting powders and the spinning and sintering parameters. In addition, it is proposed that the spinning and sintering method for hollow fibre fabrication described herein is applicable on an extensive range of MIEC materials for emerging oxygen perm-selective membrane-based technologies.

This paper brings together characterisation work based on thorough pre- and post-operation SEM-EDS/EPMA-WDS analyses of the thermal and mechanical properties of the membranes including structural characterisation (XRD). The membranes were subjected to high temperature cycling (between 750 and 950 °C) and oxygen chemical potential differences for an average operation period of up to 10 days per sample. Despite the fact that oxygen permeation measurements showed that only LSCF membranes could achieve a greater magnitude of oxygen fluxes, all membranes exhibited great chemical and mechanical stability with uniform distribution of integral perovskite elements and no foreign elements. These La-based membranes hold potential to be integrated into modules and exploited in both existing and envisaged industrial processes and commercial applications.

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1. Introduction

Mixed ionic and electronic conductors (MIECs) are perovskite-based metal oxides. They have received considerable attention over the last two decades for their potential applications in solid oxide fuel cells (SOFCs), chemical sensors, chemical reactions and gas separation [1–6]. Owing to the favourable intrinsic properties of these materials, they can simultaneously act as oxygen extractor and barriers to other species in gas mixtures at temperatures typically higher than 700 °C and under a chemical potential gradient [7–10].

Many studies have been carried out on various perovskite-based membranes, including $\text{A}_x\text{Sr}_{1-x}\text{B}_y\text{Co}_{1-y}\text{O}_{3-\delta}$ subsystems, to establish their oxygen permeation capabilities. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) and its zirconia-containing and strontium-free analogue, $\text{BaZr}_x\text{Co}_y\text{Fe}_z\text{O}_{3-\delta}$ (BCFZ) are the most promising among

these membrane systems in that they provide the highest oxygen fluxes when made into hollow fibre membranes for separating oxygen from gas mixtures [11–15]. It has been found that cation diffusion, in particular in BSCF membranes, may lead to kinetic demixing, membrane decomposition and eventual failure, all of which as a result of long exposure to a thermodynamic gradient (chemical potential gradient, temperature, or pressure) [16–19].

However, one of the most studied membrane materials in the $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ perovskite family, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (further abbreviated to LSCF), exhibits lower fluxes in favour of mechanical and chemical stability at the required operating temperatures as well as in harsh gas environments in real-life industrial applications (e.g. CO_2 , SO_2 , H_2O). Recent studies have shown that oxygen permeability was not affected by the kinetic demixing and accompanying decomposition of either the LSCF oxygen-separation membranes (after long-term operation for up to 5512 h under air separation conditions) or the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Fe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ oxygen-separation membranes (with the Co content $0 \leq x \leq 1$, operating for more than 700 h at 1150 °C) [20–24]. The $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$ (LSF) was

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tested for oxygen permeation and methane conversion and showed higher stability and higher O₂ fluxes in He and CO₂ environments than the cobalt-containing LSCF membranes [25]. Furthermore, La_{1-x}Sr_xFeO₃ was investigated in the water-gas shift (WGS) reaction for hydrogen production which showed lower strontium content offering lower oxygen permeation rates (lower oxygen vacancy concentration) [26,27]. Dense planar and tubular La_{0.5}Sr_{0.5}FeO_{3-δ} membranes studied in the partial oxidation of methane to syngas showed no degradation [28].

In this work, four lanthanum-based MIEC perovskite membrane materials have been selected: the above mentioned cobalt-based LSCF and three cobalt-free subsystems: La_{0.5}Sr_{0.5}FeO_{3-δ} (LSF), the A-site strontium-rich (and equally lanthanum deficient), B-site substituted La_{0.2}Sr_{0.8}Fe_{0.9}Zr_{0.1}O_{3-δ} (LSFZ) and La_{0.2}Sr_{0.8}Fe_{0.8}Nb_{0.2}O_{3-δ} (LSFN). The choice of LSF-related perovskites was based on their potential as oxygen separation membranes including their previously confirmed stability in reducing conditions and long-term stability (for periods of several hundred hours) as cathode materials in solid oxide fuel cells (SOFCs) [29–31]. The four MIEC membranes under study in this paper were subjected to a temperature range of 750–950 °C, laboratory air (feed side) and argon sweep gas (permeate side). Their oxygen permeation performance and stability were compared alongside the pre- and post-operation analysis results on microstructural and compositional changes.

2. Experimental

2.1. Materials

2.1.1. Powder synthesis

The ceramic oxides used for the membrane production were fabricated by spray pyrolysis by CerPoTech AS (Trondheim, Norway). Aqueous solutions of the respective precursors were prepared and mixed in stoichiometric ratios, before the stable solution was sprayed into a furnace for each material. The as-prepared powders were calcined, ball milled in ethanol with YSZ grinding media and sieved, before a final heat treatment was executed to remove organic residues from powder processing. Relatively low calcination temperatures were chosen to avoid particle coarsening and maintain powders with high sintering activity. The drawback of this is minor amounts of carbonate and binary oxide residuals in the as-prepared powders. When prepared with the correct stoichiometry the materials form a single phase upon sintering.

2.1.2. Capillary membrane production

The dense gas-tight capillary membranes were manufactured using an adapted spinning and phase inversion method followed by calcination and sintering. The suspension preparation method, previously used for polymeric membranes in VITO, was modified by adjusting the polymer/solvent/non-solvent system and the amount of perovskite powder added to the starting polymer suspension [32–34]. In brief, the spinning method involves extruding the powder suspension through the outer orifice of a spinnerette into a non-solvent bath while the non-solvent runs through the inner orifice. Non-solvent induced phase inversion (i.e. solidification) of the nascent capillary occurs as the polymer with solvent precipitates from the continuous stream of the powder suspension. All the membranes reported here were spun from a dope comprising the perovskite powder in cellulose acetate (CA, Mr ~52,000, Fluka), dimethylsulphoxide (DMSO, Synthesis grade, Merck), de-ionised water as the phase-inversion polymer (binder), and a solvent and non-solvent additive to the polymer solution. The polymer solutions were prepared by dissolving CA in DMSO/

de-ionised water mixtures at 65 °C. The DMSO/H₂O ratio for different polymer concentrations was varied to obtain the maximum water addition before precipitation of the polymer. Subsequently the optimal polymer/solvent/non-solvent composition was set to 16/87-13 where the solution contained 16 wt% of polymer of the total amount of polymer, solvent and non-solvent, 87 wt% of solvent and 13 wt% of non-solvent of the total amount of solvent and non-solvent.

Ceramic powder suspensions of similar viscosities were prepared by mixing 10% CA16/87-13 by weight with 90% of each of the four selected powders and 1 wt% glycerol using a planetary centrifugal mixer (Thinky Mixer ARE-250). Prior to mixing, the powders were milled in acetone or water in a Planetary Ball Mill (15' 200 rpm, ZrO₂-Yr₂O₃ grinding balls 3 mm and then sieved through a 90 μm mesh) to break down coarse agglomerates.

The powder suspension was then extruded through a tube-in-orifice spinneret into a coagulation bath where immediate precipitation of the capillaries took place in a mixture of 50 vol% de-ionised water and 50 vol% glycerol. The air gap between the spinneret and coagulation bath was kept at 2.5 cm, while the capillaries were formed by being pushed out of the spinneret at 5 m/min and at about 4 bar. Phase-inversion at the lumen side of the capillaries was induced by applying a bore liquid mixture of 50 vol% de-ionised water and 50 vol% glycerol. After solidification the capillaries were washed out by de-ionised water and dried in air at room temperature.

Final formation of the ceramic capillaries was carried out by calcination and sintering the “green body”. The effect of the viscous deformation occurring at the first stage of the thermal treatment was also investigated, the extent of which was shown to be related to the rheology of the particle loaded polymer (described in the literature) [35]. For the fine B-site substituted powders used in this work the viscous deformation occurs at a particle-specific temperature and for a specific period of time (typically at about 200 °C for 4 h). Calcination for all four powder-binder systems needed to be performed as a separate and slow (10–20 °C/h) process for the cellulose acetate binder burn-off at 600 °C for 1 h. The calcined capillaries were further sintered to obtain high-density membranes. Sintering times and temperature profiles ranging from 1250 to 1350 °C for 4 h were optimised for each powder type in order to vary their final density and mechanical strength.

For the sake of comparison, a few LSCF test membranes were prepared by an alternative phase inversion method with polyetherimide and N-methyl-2-pyrrolidone (PEI/NMP) polymer/solvent system (described elsewhere) [36,37] and sintered to 1300 °C (skipping the calcination step).

2.2. Characterisation

Brunauer–Emmett–Teller (BET) surface area analyses were performed on as-received and milled powders using a NOVA 3000-Series Quantachrome nitrogen adsorption analyser. The rheologies of the suspensions were determined using a Haake-Mars rotational rheometer with a plate-to-plate configuration and a gap of 0.400 mm at 25 ± 0.1 °C and with both increasing and decreasing shear rates from 0.01 to 30 s⁻¹ in a time interval of 300 s each.

Dilatometric measurements have been made on the 10 mm cut sintered capillary samples by a Netzsch DIL402C dilatometer from room temperature up to the point just before melting (1200 °C), using the same heating rate of 2 °C/min and atmospheres (air and argon) as those used in the furnace for oxygen permeation experiments. The coefficients of thermal expansion (CTEs) over a temperature range from room temperature to 1000 °C were

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