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Fabrication of perovskite capillary membranes for high temperature gas separation

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ABSTRACT

Oxygen-permeable perovskites with mixed ionic–electronic conducting properties can play an important role in carbon capture and storage techniques. Their ability to separate oxygen from air is needed, more specifically, in oxy-fuel and pre-combustion technologies. In this work, the first detailed comparative analysis and new results are reported on four types of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) capillary membranes: non-coated sulphur-containing; catalyst-coated sulphur-containing; non-coated sulphur-free and catalyst-coated sulphur-free. The fabrication of BSCF capillaries by a spinning technique based on phase inversion is further discussed and their oxygen separation performances are interpreted. The comparison of the performance of these different generations of BSCF capillaries of similar dimensions demonstrates a significant impact of the sulphur contamination on both the oxygen flux through the membrane and the activation energy of the overall oxygen transport mechanism. Careful attention is paid to the effect of activation layers on both sulphur-free and sulphur-containing types of capillaries. Additional long-term testing of the sulphur-free BSCF capillaries is presented, where partial decomposition of the membrane surface was observed due to kinetic demixing.

1. Introduction

Oxygen production and partial oxidation are two emerging applications of ceramic membranes. Oxygen-permeable perovskites with mixed ionic–electronic conducting (MIEC) properties can play an important role in the high temperature separation of oxygen from air. When such gastight materials are exposed to an oxygen chemical potential gradient at temperatures typically higher than 700 °C, they selectively transport oxygen in the form of oxygen ions from the high partial pressure side to the low partial pressure side of the membrane, without the need for electrodes and an external electrical load. These oxygen separating membranes have great potential for the capture and removal of CO_2 in oxy-fuel and pre-combustion technologies in fossil fuel power plants [1–4]. Since large-scale gas separation applications demand high membrane surface/volume ratios, membranes with capillary or hollow fibre geometry have a distinct advantage over tubular and flat sheet membranes. Besides membrane stability under operating conditions, the oxygen flux through a membrane needs to be sufficiently high for it to be economically interesting. $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) shows one of the highest oxygen fluxes of all known perovskite MIEC materials [5–8], which is why it was chosen for the development of dense and gastight capillary membranes.

In this work, a detailed comparative analysis and new results are reported on four different types of BSCF capillary membranes: non-coated sulphur-containing; catalyst-coated sulphur-containing; non-coated sulphur-free and catalyst-coated sulphur-free. The fabrication of these capillaries by a spinning technique based on phase inversion is further discussed and their oxygen separation performances are interpreted. The spinning technique, commonly used for polymeric membranes in VITO, has been modified for the purpose of this work by adjusting the amount of BSCF powder added to the starting suspension. It has already been shown that the rheology of the ceramic suspension and the composition of the bore liquid and coagulation bath are key factors for making macrovoid-free green capillaries [9]. However, in the first generation of the BSCF capillaries (i.e. the non-activated sulphur-containing ones) the oxygen permeation fluxes through these membranes were much lower than reported in literature due to the formation of stable $BaSO_4$ at the membrane surface [9–12].

Two different strategies were followed to avoid the effect of sulphur on the oxygen flux: surface activation of the membrane

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with a suitable catalyst [13], and development of a sulphur free phase-inversion spinning system [14–16]. The comparison of the performance of these different generations of BSCF capillaries of similar dimensions shows the effect of sulphur contamination on both the oxygen flux through the membrane and the activation energy of the overall oxygen transport mechanism. In addition, the effect of activation layers on the sulphur-containing as well as sulphur-free capillaries will be presented here. It has also been confirmed that the contribution of the surface exchange kinetics to the overall oxygen transport process increases at lower temperatures for all the presented capillary generations.

Another challenge is the long-term stability and performance of the BSCF capillary membranes [7,14,17]. In this work, long-term testing of the stability of a sulphur-free BSCF capillary at temperatures as low as 750 °C was explored, revealing reaction and partial decomposition of the membrane surface due to kinetic demixing and decomposition. The bulk of the membrane, however, shows a homogeneous distribution of BSCF elements.

2. Experimental

2.1. Materials

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ powder (specific surface area 1.2 m^2/g, d_{50} = 3 μm, HITK Hermsdorfer Institut für Technische Keramik) was ball-milled for either 4 or 16 h in acetone prior to use. After milling, the particle size distribution of the BSCF powder was measured in water (Mastersizer X, Malvern), while the specific surface area was determined by the Brunauer–Emmet–Teller (BET) method calculated from nitrogen sorption isotherms at −196 °C (Quantachrome Autosorb-1-MP). The phase composition of the milled BSCF powder was examined using an X-ray diffractometer (Philips X'Pert PRO). For synthesis of the sulphur-containing BSCF capillaries, polysulfone (P-1800 NT 11, Solvay Advanced Polymers) and N-methyl-2-pyrrolidone (M-PYROL, ISP Technologies) were used as a binder and solvent, respectively. For synthesis of the sulphur-free capillaries, cellulose acetate (Mr ~52,000, Fluka), dimethylsulphoxide (synthesis grade, Merck) and de-ionised water were used as phase-inversion polymer, solvent and additive to the polymer solution, respectively. Glycerol (technical grade, VWR) was used as an internal coagulant. De-ionised water or a mixture of 50 vol% glycerol and 50 vol% de-ionised water were used as an external coagulant.

2.2. Preparation of BSCF capillaries

The BSCF capillaries were prepared as described in [9,13,14]. In short, polysulfone (PSf) solutions were prepared by slowly dissolving PSf in N-methyl-2-pyrrolidone (NMP) and leaving the mixture to stir for 1 h at a speed of 600 rpm using a high speed mixer (DiSSMAX, Molteni). Sulphur-containing BSCF suspensions were prepared by mixing PSf solutions with the milled BSCF powder using a planetary centrifugal mixer (Thinky Mixer ARE-250). Prior to spinning, each suspension was degassed under vacuum for half an hour at room temperature. Then, the suspension, pressurised to 4 bar, was extruded through a tube-in-orifice spinneret into a coagulation bath where solidification of the capillaries took place in de-ionised water or a mixture of 50 vol% glycerol–50 vol% de-ionised water.

Sulphur-free polymer solutions were prepared by dissolving cellulose acetate (CA) in dimethylsulphoxide (DMSO)/deionised water mixtures at 65 °C. The DMSO/de-ionised water ratio for different polymer concentrations was varied in order to obtain the maximum water addition before the precipitation of the polymer occurred, which was visually checked by the transition of the polymer solution from translucent to turbid. This technique was used to determine the binodal of the ternary phase diagram for the CA/DMSO/water system. Sulphur-free BSCF suspensions were then prepared by stirring a CA solution with the BSCF powder and glycerol in the Thinky Mixer ARE-250.

Prior to spinning, each suspension was degassed under vacuum for half an hour at room temperature. Then, the spinning suspension, is passed through a tube-in-orifice spinneret, at a pressure of 4 bar, into a coagulation bath containing de-ionised water or a mixture of 50 vol% glycerol–50 vol% de-ionised water where solidification of the capillaries took place.

The experimental spinning setup is shown in [9,18]. The spinneret and coagulation bath were separated by an air gap of 3 cm where the capillaries were emerging at 5.5 m/min. Phase inversion at the inside of the capillaries was induced by applying glycerol as bore liquid. After coagulation, the capillaries were washed out of any remaining solvent in de-ionised water, and then dried in air at room temperature. The ceramic capillaries obtained their final properties by removing the binder during a slow calcination step in air at 600 °C and afterwards a sintering step at 1100 °C for 5 h.

The membrane surfaces were coated with praseodymium oxide (PrO_x) following the surface modification procedure described in [13]. This procedure included an immersion of a selected capillary into a saturated solution of $Pr(NO_3)_3$ in C_2H_5OH at room temperature for 5 min, subsequent drying at 70 °C for 2–3 h and repetition of the steps above, followed by the final annealing step at 1100 °C for 5 h. A similar Pr-catalyst layer of 1.0 ± 0.1 mg/cm^2 (~6 μm thickness) on the outer membrane surface was obtained for both the PrO_x activated BSCF capillaries: sulphur-containing and sulphur-free.

2.3. Characterisation of BSCF capillaries

The rheology of the ceramic suspensions was measured using a plate-to-plate sensor with a gap of 0.400 mm at 25 ± 0.1 °C (Haake Mars). The viscosity of each suspension was first measured with increasing shear rates from 0.01 to 30 s^{-1} in a time interval of 300 s, which was immediately followed by decreasing shear rates from 30 to 0.01 s^{-1} over the same time interval. Since the suspension was already exposed to high shear rates when leaving the spinneret, it was sufficient to consider only the viscosity data for the decreasing shear rates [9].

The gas-tightness tests on the sintered capillaries were performed using an automated capillary flow porometer (CFP-1200-A, PMI) as described in [9,14]. The mechanical strength of the sintered BSCF capillaries was assessed by the flexural strength, based on the four-point bending test using an Instron 5582 Universal Testing Machine. The cross-sections, outer and inner membrane surfaces were examined using a JEOL JSM-6340F field emission scanning electron microscope (FESEM) with energy dispersive spectrometry (EDS). Spatial mapping of the membrane composition by electron probe micro-analysis (EPMA) was carried out using a Jeol Superprobe JXA 8621 fitted with three wavelength dispersive spectrometers (WDS) and an energy dispersive spectrometer (EDS), operating at an accelerating voltage of 15 kV and probe current from 1 to 10 nA.

2.4. Oxygen permeation measurements

The oxygen permeation fluxes through gastight BSCF capillaries (of thickness ~0.4 mm, outer diameter ~3.5 mm and ~30 mm length) were recorded as a function of sweep gas (Ar) flow rate and temperature range of 800–950 °C using the experimental setup already presented in [9,13,14]. Synthetic air was passed through the shell side of the capillary at a rate of 100 ml/min, while argon with known oxygen partial pressure $p(O_2) \approx 5$ Pa was applied through the core side of the capillary. The oxygen partial pressure in the