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Effect of forming techniques on efficiency of tubular oxygen separating membranes

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ABSTRACT

Two dense thin-walled tubular membranes used to separate oxygen from air manufactured from a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) mixed oxide with perovskite-like structures were synthesized by both extrusion and isostatic pressing methods. The properties of the sintered membranes (the apparent density, the apparent porosity, the water absorbability, the chemical composition, the crystallographic structure and microstructure, and the oxygen mobility) that affect oxygen permeation through the membranes were determined. Both manufactured membranes were capable of separating oxygen from air. The highest oxygen permeation flux (2.33 cm^3 O_2/(cm^2 min)) was obtained using the membrane synthesized by extrusion at 950 °C under 2 dm^3/min air flow and 5 dm^3/min of helium flow. The effect of the pressure used during the synthesis of the membranes on the properties of the membranes is discussed. The influence of air quantity delivered to the system on the oxygen permeation flux for both membranes at 950 °C and constant helium flow was also determined. Extrusion was found to be an attractive method to manufacture industrial-scale membranes that separate oxygen from air.

1. Introduction

Mixed oxides with perovskite-like structures and both ion and electron conductivities are used to manufacture dense membranes that separate clean oxygen from air. The effectiveness of these membranes as measured by the oxygen flow permeating through the membrane depends on the chemical composition of perovskite material, the method used to manufacture the membrane (extrusion or isostatic pressing), the thickness of the membrane (controlled by diffusion or surface processes), the membrane's microstructure, the operating temperature of the membrane and the gradient of oxygen partial pressures at both sides of membrane [1,2].

Most reports regarding mixed conducting ceramic membranes involve disk-shaped perovskite-type membranes for which the effective area is very limited. For industrial applications, dense tubular membranes with high mechanical stability, effectiveness and ease of application should be prepared [3,4]. Usually two methods are used to prepare dense tubular membranes, namely, the plastic/thermoplastic extrusion method [3–7] and the isostatic pressing method [8,9]. When the isostatic pressing method is used, only simple shapes with green bodies can be prepared, but this technique creates an uniform distribution of hydrostatic pressure from all directions and achieves a higher and more uniform density of the material [3]. Conversely, the extrusion method has a lower cost and can be used to create complicated shapes [6]. Additionally, centrifugal casting [10] or slip casting [11] methods can also be used to prepare dense oxygen membranes. Finally, rather than a disk-shaped membrane, there have also been attempts to produce a tubular membrane consisting of a porous support from perovskite material, a dense membrane and an activation layer [12].

Similar to disk-shaped membranes, the size of the dense membrane has a major impact on the oxygen permeation flux through a tubular membrane. The oxygen permeation flux is inversely proportional to the tube length and its thickness. Therefore, taking into account the efficiency of oxygen separation processes required for practical applications, it is necessary to obtain a tube with an optimal length and a wall of minimal thickness while maintaining the appropriate mechanical properties of the membrane [8]. Based on literature analysis, presently manufactured tubular dense oxygen membranes possess external diameters of 5–10 mm, the wall thicknesses of 0.3–1.75 mm and lengths up to 150 mm [3–6,8,10].

Currently, cryogenic air separation is the best available technology

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used in large-scale oxyfuel power plants [13]. However, an air separation unit (ASU) based on perovskite oxygen membranes has been suggested as a promising alternative to the cryogenic method [13]. A scheme of an oxyfuel power plant integrated with an ASU in which an oxygen membrane module was used has been proposed by Hashim et al. and Stadler et al. [14,15]. To be effective in commercial oxy-combustion applications, the oxygen membrane must exhibit a high oxygen permeation flux. Additionally, the manufacturing process of the dense tubular oxygen membranes must be well developed and efficient.

In this paper, the preparation of dense BSCF tubular membranes by both extrusion and isostatic pressing methods is described. Both types of membranes are characterized and their properties are compared. The aim of this work was to determine the effect of the manufacturing process on the properties of the membrane.

2. Materials and methods

A $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ mixed oxide powder with a perovskite-like structure was synthesized by the solid state method from the appropriate metal oxides: Co_2O_3 (minimal content of Co 70%, SIGMA), Fe_2O_3 (99% of purity, Sigma-Aldrich) and metal carbonates: $BaCO_3$ (99,5% of purity, Chempur), $SrCO_3$ (99% of purity, Chempur). The raw materials were mixed with ethyl alcohol and milled in a mixer mill for two hours. The obtained powder was calcined in an electrical furnace for five hours at 950 °C. The triple milling and calcinations were necessary to obtain a single phase material. A detailed description of the properties of the BSCF powder can be found in our previous paper [16].

The oxygen membranes were manufactured by both extrusion and isostatic pressing. For the preparation of the membrane by extrusion the following procedure was used. A suspension of methylcellulose (Ashland, 10 wt%) in a mixture of water and oil emulsion F15 (Naftochem, 20 wt%) was prepared. The plastic body was prepared from 1.7 kg of a methylcellulose suspension and 10.4 kg of the BSCF powder in a device consisting of a bowl and a mixer for body homogenization (Spomasz).

A vacuum worm press type V10/3 (DORST) equipped with a water jacket for cooling the plastic body was used for tubular membrane extrusion. While the plastic body was forming, it was under a vacuum of 0.1 bar. Therefore this device forms membranes with the highest apparent density after sintering. The temperature of the water in the water jacket was 10 °C. The velocities of the feeding and pressing worms were 6 and 5 min^{-1}, respectively. The temperature and pressure in the press chamber during the extrusion of the BSCF plastic body were controlled in four points of the pressing cylinder. The temperature rose from 27 to 38 °C while the pressure diminished from 60 bar in the inlet part of pressing worm to 10 and 5 bar in the middle part of pressing cylinder to 4 bar near the shaping tools. As a result of this formation process, green tubes with lengths of 600 mm, external diameters of 23.4 mm and internal diameters of 17.4 mm were obtained. The green tubular membranes were placed on profiled wood supports to maintain the shape of the tubes during extrusion and to protect them against deformation. The tubular membranes were dried in the air for 24 h and then in the dryer at 70 °C for 4 h. The dried tubes were cut to the appropriate length, and then a hole was created to hang the tubes in a furnace during sintering. The dried green tubular membranes were sintered in an electrical furnace according to the curve ensuring high density of sintered material. The highest sintering temperature was 1100 °C, the dwell time was 5 h, and the rate of heating and cooling was 100 °C/h. The next stage of membrane extrusion was to machine the membrane via grinding. This resulted in a membrane wall thickness of 1.0 mm. Two flanges at the end of the tubes were required to assemble the membrane, and the membrane was sealed for membrane testing. The membrane prepared by extrusion was denoted as ET.

The second method used to form tubular membranes was via isostatic pressing. Manufacturing tubular membranes by this method required determining the optimal parameters to use for pressing, turning the semi-product on the lathe, development of the sintering curve and finally grinding the sintered membrane. To improve the mouldability, the raw material – the perovskite-like powder – was granulated. To granulate the powder, it was mixed with deionized water in a mixer mill for 30 min, and then dispex (10 wt%), oil emulsion F15 (20 wt%) and polyvinyl alcohol (10 wt%) were added. The granulation procedure was performed in a spray drier (Niro) under the following conditions: an inlet temperature of 220 °C, an outlet temperature of 80 °C and a spray pressure of 40 mm water column [16].

To shape the membrane, the BSCF granulate was pressed under a pressure of 2500 bar using a steel arbor and an elastic form made of silicone material. Next, the semi-product was turned on a lathe, and the resulting wall thickness of the membrane was 2.35 mm. The membrane was sintered at 1050 °C, the dwell time was 5 h, and the rate of heating and cooling was 100 °C/h. The sintered membrane was then grinded similarly to the membrane synthesized via extrusion. The membrane synthesized by isostatic processing was denoted as IPT.

The basic properties of both types of sintered tubular membranes were analysed. Parameters characterizing the extent of material sintering (i.e., the apparent density, the apparent porosity and the water absorbability) were estimated by a method that uses Archimedes' law. The chemical composition of materials was determined by ICP analysis (Liberty 220 Varian). XRD patterns were obtained using X'Pert PRO PANalytical powder diffractometer, and the lattice parameters were calculated using a DICVOL programme using the FullProf Suite package. The surface microstructure of the materials was analysed using scanning electron microscopy SEM/HITACHI S-3400N/2007.

The temperature programmed desorption of oxygen ($TPDO_2$) was conducted in a flow quartz reactor. Samples (100 mg) of crushed membranes (and of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ powder) were pretreated in a flow of O_2 at 500 °C for 1 h. The samples were then cooled to 40 °C and placed in a He stream for 0.5 h. Subsequently, the $TPDO_2$ experiments were performed by heating the samples to 950 °C at a heating rate of 10°/min under flow of He (30 ml/min). The effluent gas was analysed for O_2 using a mass spectrometer (OmniStar QMS 200, Pfeiffer Vacuum) by monitoring the m/e signal at 32 (O_2).

The oxygen permeation of the dense tubular membranes was measured using a home-made experimental set-up (Fig. 1). The basic element of this installation was a tubular electric furnace, which ensured appropriate temperatures for testing and enabled control of the time and the speed of heating and cooling. The testing section was located inside the furnace. The furnace was composed of a quartz tube 50 mm in diameter. The testing section (an alumina tube 28 mm in diameter placed on its axis) was placed inside the furnace. The tested tubular oxygen membranes were fixed to the alumina tube using a ceramic glaze, and they were immobilized using a tightening system.

The oxygen permeation flux through both the ET and IPT membranes at temperatures ranging from 700 to 950 °C and constant processing gas flows was determined. As the sweeping gas, helium was applied, and the flow rate was set to 1000 ml/min. Synthetic air was introduced to the system at a speed of 2000 ml/min. The oxygen concentration in the outlet gas was determined by gas chromatography (Varian CP-4900). The volume flow of outlet gas was estimated using a pellicular electronic flow meter, and then the data were recalculated for standard conditions. A scheme of the apparatus used to determine the oxygen permeation flux through the tubular membranes is presented in Fig. 1.

Additionally, the influence of air quantity delivered to the system on the oxygen permeation flux and constant helium flow for both membranes were also estimated. The oxygen utilization (UT_{OX}) was calculated as the amount of oxygen permeating through membrane