Journal of Membrane Science 377 (2011) 198–205

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Ultrahigh oxygen permeation flux through supported $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes

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ARTICLE INFO

Article history:
Received 20 January 2011
Received in revised form 21 April 2011
Accepted 24 April 2011
Available online 30 April 2011

Keywords:
Oxygen transport membrane
Supported membrane
Oxygen flux
BSCF
Oxygen separation

ABSTRACT

Oxygen transport membranes made of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) were manufactured by tape casting and co-firing. The disk-shaped membranes consisted of a top gastight layer (70 μm thick) and a porous substrate (830 μm thick) with 34% open porosity. The variation of the permeation operation conditions allowed (i) the identification of the different limitations steps in the permeation process, i.e., bulk oxygen ion diffusion, catalytic surface exchange and gas phase diffusion in the membrane compartments and porous substrate, and (ii) the ultimate optimization of the oxygen flux. The variables considered in the systematic permeation study included the inlet gas flow rate of the sweep and air feed, the temperature and the nature of the oxygen feed gas (air or pure oxygen). Moreover, the influence of the deposition of a catalytic activation layer (17 μm thick) made of BSCF on top of the thin gastight layer was investigated. As a result of this parametric study, unpreceded oxygen flux values were achieved, i.e., a maximum flux of 67.7 ml(STP) min^{-1} cm^{-2} was obtained at 1000 °C using pure oxygen as the feed and argon as the sweep, while a flux of 12.2 ml(STP) min^{-1} cm^{-2} at 1000 °C was obtained when air was used as the feed.

1. Introduction

One important strategy for reducing CO_2 emissions, while the energy demand is increasing, is carbon capture and storage (CCS). Different fossil fuel power plant concepts for CCS are currently being developed. Examples include post-combustion, pre-combustion and oxyfuel. In oxyfuel power plants, the fossil fuel is combusted using pure oxygen or a nitrogen-free gas stream enriched with oxygen. The result of this concept is an off-gas containing primary CO_2 and H_2O, i.e., 90–95% CO_2 in the dried flue gas. The CO_2 can then be captured more easily than when air is used in the combustion process, which leads to 10–14% CO_2 in the dried flue gas [1]. The oxygen required for this concept can be provided by different methods, of which ceramic oxygen transport membranes[1] (OTMs) have the lowest efficiency losses [2], especially when recirculated flue gas is used as sweep gas.

OTMs consist of gastight mixed ionic-electronic conductors (MIEC) and allow oxygen diffusion via oxygen vacancies in the crystal lattice. Therefore, the selectivity of the membranes is infinite, which means that they provide pure oxygen. The most promising materials for OTMs are perovskites with the formula $ABO_{3-\delta}$ [3]. In last decade, intensive research has been dedicated to the preparation and characterization of MIEC membranes [4–12]. The materials showing the highest oxygen permeability are based on $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), which was first reported by Shao et al. [13] and has attracted great interest recently [14–18]. The thermodynamic driving force for oxygen transport through a MIEC membrane is the oxygen chemical potential gradient along the thickness of the membrane, which is given by the operating conditions. The oxygen permeation flux based on bulk diffusion can be described by the Wagner Equation [3]:

$$J_{O_2} = \frac{RT}{16F^2L} \int_{P''_{O_2}}^{P'_{O_2}} \sigma_{amb}(pO_2)d \quad \ln \quad pO_2 \tag{1}$$

where J_{O_2} is the oxygen permeation flux in mol m^{-2} s^{-1}, R is the gas constant, F is the Faraday constant, L is the membrane thickness, σ_{amb} is the ambipolar conductivity, and P'_{O_2} and P''_{O_2} are the oxygen partial pressures at the high pressure side and low pressure side, respectively.

In order to increase the oxygen permeation flux through a membrane, the thickness should be as low as possible. When the thickness becomes very low, a porous support is needed for mechanical stability, particularly in the case of planar membranes. This has led to recent increased interest in the development of supported membranes. The membranes that have been investigated vary widely in terms of membrane thickness (10–500 μm)

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[1] Also called ionic transport membranes (ITMs).

0376-7388/$ – see front matter
doi:10.1016/j.memsci.2011.04.050

Table 1
Overview of literature data for asymmetric membranes.

Membrane material	Layer thickness (μm)	$j^{\text{asymmetric}}$ (ml min^{-1} cm^{-2})	$j^{\text{asymmetric}}$ / j^{bulk}	$L^{\text{bulk}}/L^{\text{asymmetric}}$	T (°C)	Source
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$	200	0.2	3.3	10.0	800	18
$SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_3$–0.4MgO	200	0.3	10.0	6.0	900	19
$Sr_{1-x}Fe(Al)O_3$–$SrAl_2O_4$	500	0.4	4.0	2.0	900	20
$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$	20	0.1	1.9	50.0	900	21, 11
$SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_3$	200	1.0	1.9	7.5	900	22
$La_{0.6}Ca_{0.4}CoO_3$	10	1.5	4.4	100	900	23
$La_{0.8}Sr_{0.2}Fe_{0.7}Ga_{0.3}O_3$	80	0.016	5.0	12.5	900	24
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$	120	1.94	1.3	8.3	900	25

and material [19–26] (Table 1). The permeation enhancements that have been reported are normally much less than the values predicted by the Wagner equation (1), assuming direct reciprocal behaviour of membrane thickness and permeation rate. This is due to the fact that Wagner's theory is only valid for solid state diffusion; it does not include surface exchange kinetics (O_2 adsorption, dissociation and reduction) or other gas-phase phenomena, which at least partly dominate permeation through thin membranes. Furthermore, a limiting influence of the porous support has to be considered [26].

This work presents the preparation of asymmetric membranes made of BSCF. The systematic study of the membrane operation variables (inlet gas flow rate at the two membrane compartments, temperature and the nature of the oxygen feed gas) and their influence on the oxygen flux is discussed. Moreover, the influence of the application of an activation layer on top of the thin gastight layer is investigated. The oxygen flux is optimized by eliminating the different process limitations step by step.

2. Experimental

2.1. Membrane preparation

Both the membrane layer and the support were manufactured by tape casting using BSCF. This approach has several advantages, such as perfect chemical compatibility and the same thermal expansion of the two layers [22]. The commercial BSCF powder used (Treibacher Industrie AG, Austria) exhibited an average grain size of 1.7 μm. In the support, corn starch (Cargill, Germany) was used as the pore former with a particle size in the range of 2–30 μm [27].

The slurry preparation procedure is shown in Fig. 1 and was performed according to [28]. Two slurries were prepared: the slurry for the support layer contained 20% corn starch in relation to the total solid content, whereas the slurry for the membrane layer did not contain any pore former. Sequential tape casting was used to prepare the membrane. First, the membrane layer was cast in two steps with a drying step in between using casting gaps of 50 μm and 100 μm, respectively. After drying, the support layer was cast on top of this layer with a casting gap of 1.9 mm. This layer was then dried and the samples were cut out of the green tape, debindered and sintered in air at 1100 °C for 3 h.

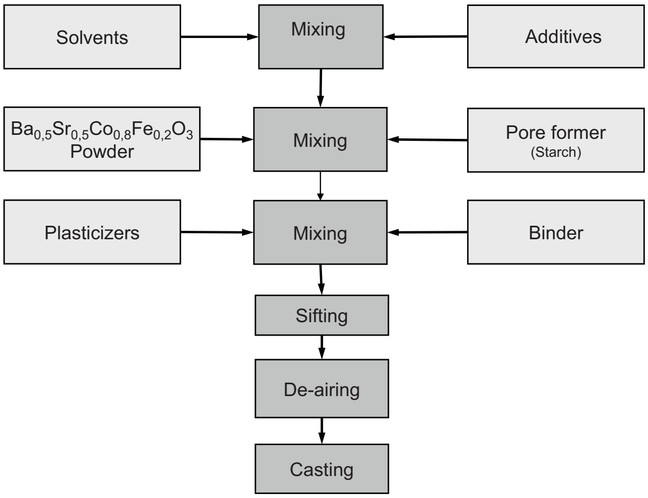

Fig. 1. Slurry preparation for tape casting.

The oxygen activation layers were prepared via screen printing. The screen printing ink consisted of BSCF powder provided by Fraunhofer IKTS (Hermsdorf, Germany). It was ball-milled in an acetone suspension prior to preparation of the screen-printing inks and an average particle size of 250 nm was achieved. A typical additive containing 94 wt.% terpineol and 6 wt.% ethylene cellulose was used. Further homogenization was conducted using a three-roll mill. In order to complete homogenization, this step was repeated three times. Moreover, graphite (Aldrich) was used as the pore former in the screen-printing ink. The printed layer was sintered at 1010 °C.

The microstructure was investigated using scanning electron microscopy (SEM) (Zeiss Ultra 55), and elemental analysis was carried out with energy-dispersive X-ray spectroscopy (EDS) (INCA, Oxford). The porosity of the membranes obtained was investigated by light microscopy and quantitative image analysis using commercial software, i.e., ImageJ and analySIS. Gas tightness was measured using He leakage (Pfeiffer vacuum).

2.2. Oxygen flux measurements

Oxygen permeation studies were carried out in a lab-scale quartz reactor. Synthetic air (21%, v/v O_2 in the feed stream) or pure oxygen was fed into the oxygen-rich chamber, while argon was used as the sweep gas on the permeate side. Both gases were fed at atmospheric pressure. Inlet gases were preheated in order to ensure the correct gas temperature for contact with the membrane surface. This is particularly important when high gas flow rates are employed. All streams were individually mass flow controlled. The temperature was measured by a thermocouple attached to the membrane. A PID controller maintained temperature variations within 2 °C of the set point. The samples consisted of gastight supported BSCF membranes and membrane gas leak-free conditions were achieved using gold rings on both sides of the membrane, which were heated to 1010 °C for 4 h immediately prior to the measurement. The permeate was analysed at steady state by online gas chromatography using a micro-GC Varian CP-4900 equipped with Molsieve5A, Pora-Plot-Q glass capillary, and CP-Sil modules. Membrane gas leak-free conditions were ensured by continuously monitoring the nitrogen concentration in the product gas stream (just before and after switching to a pure O_2 feed). An acceptable sealing was achieved when the ratio between the oxygen flow leak and the oxygen flux was lower than 1%. The data reported here were achieved at steady state after 1 h in the reaction stream. Each test was repeated three times to minimize the analysis error. The experimental analytical error was below 0.5%.