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# Oxygen permeability and phase stability of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ perovskite at intermediate temperatures

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## ABSTRACT

The oxygen permeation flux through $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) membranes of different thicknesses (1.5–2.5 mm) was measured between 800 and 900 °C under vacuum conditions. The vacuum pressure at the permeate side of the membranes was varied from 5 mbar to 30 mbar. In order to examine the effect of membrane configuration, an asymmetric BSCF membrane with a thin-film layered structure was produced. A significant improvement in oxygen permeability was observed in the asymmetric membrane, which showed an oxygen flux of 32.45 ml $min^{-1}$ $cm^{-2}$ [STP] at 900 °C, much higher than that of dense membranes. The long-term permeation study showed that the membrane properties of the BSCF material undergo gradual deterioration at 800 °C due to phase decomposition. The hexagonal phase formed primarily in grain boundaries, and after the saturation of boundary nucleation sites, phase transition also occurred within the matrix. The SEM micrographs of BSCF membranes operating over long periods exhibit more rapid deterioration at the air feed side than at the oxygen-lean side.

## 1. Introduction

Mixed ionic and electronic conducting (MIEC) membranes have been implemented in versatile applications over the last few decades in the fields of oxygen separation, solid oxide fuel cells and partial oxidation processes of natural to synthetic gas [1–3]. In the case of oxygen generation, the perovskite-type system exhibits the highest oxygen permeation flux and remarkable mixed conductivity over a wide temperature range [4,5]. However, the structure of these oxygen permeable conductors generally deviates from ideal perovskites at high temperatures and is simply represented as $ABO_{3-\delta}$. Under this condition, oxygen transport through the membrane becomes possible via oxygen vacancies formed in the anionic sublattice as a result of balancing electrical neutrality.

The major task of membrane technology is to improve the oxygen permeability of material on the basis of reserving its durative structural stability with the aim of sustaining long-term operation. Shao et al. found that a proper introduction of barium into $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) manifestly improved the phase stability and oxygen permeability of the material [6,7]. Thereafter, perovskite-structured systems $(Ba,Sr)(Co,Fe)O_{3-\delta}$, especially with the optimized composition of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), attracted broad interest as promising membrane materials for oxygen generation. Many previous works have investigated the oxygen permeability of dense BSCF membranes as a function of membrane thickness, temperature and oxygen partial pressure, etc. [8–11]. In order to further enhance membrane permeability, Kovalevsky et al. produced a three-layer asymmetric BSCF membrane with one dense and one porous layer on the top of a thick porous support [12]. A significant increase in oxygen flux was observed compared to the dense membrane. Accordingly, the fabrication of asymmetric membranes is considered an effective route to maximize the oxygen permeability of membrane.

Despite the good performance of BSCF materials in oxygen separation, phase transition has been reported at intermediate temperatures (ITs) of 750–825 °C in accordance with a slow degradation of membrane properties [7,13]. Based on the study of long-term decomposition in BSCF, Arnold proposed that the hexagonal phase formed during operation at 800 °C because of a reversible rearrangement of the $AO_3$ layer stacking sequence, which is driven by the change in oxidation state as well as the spin-state configuration of cobalt ions [14]. In contrast, good oxygen permeation stability has been confirmed for BSCF at temperatures higher than 850 °C [15,16].

In our study, we systematically investigated the oxygen permeation flux of BSCF membranes at ITs in dependence on the membrane thickness and the oxygen partial pressure gradient. In order to assess the influence of membrane configuration, the oxygen permeability of an asymmetric membrane with a dense BSCF layer on a porous substrate of the same material was measured under vacuum conditions. In view of the limited information on the long-term performance of BSCF, the permeation stability of dense membranes at 800 °C was also studied under air/He oxygen partial pressure gradient.

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## 2. Experimental

### 2.1. Membrane fabrication

Disk-shaped $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) membranes of 15 mm in diameter were prepared by uniaxial pressing under an isostatic pressure of 125 MPa. The die-pressed green disks were sintered in static air at 1000 °C for 10 h with a heating and cooling rate of 5 K $min^{-1}$. The density of the sintered membranes was determined by the Archimedes method in ethanol and only membranes with a relative density higher than 90% were used in our studies. Prior to any experiments, both sides of the membrane were polished with silicon carbide abrasive paper (♯1200) to ensure geometrically flat surfaces. The asymmetric BSCF membrane was produced by tap casting. A 1.9 mm porous substrate of BSCF was cast on top of a 50 μm thin-film layer of the same material. In this case, possible problems of thermal mismatch and chemical reaction between the coated layer and the substrate at high temperatures were excluded by using the same BSCF material for layer and substrate. After drying, the whole membrane was co-fired at 1100 °C for 3 h in air. The sintered asymmetric membrane has a layer thickness of 20 μm and the support thickness of 900 μm.

### 2.2. Vacuum permeation measurement

The vacuum permeability of membranes was investigated by a reactor unit schematically depicted in Fig. 1. Membrane disks were sealed with two gold gaskets of 1 mm in thickness between quartz glass tubes to avoid leakage and radial contribution to the oxygen permeation flux. An external load from a compressed spring on the glass tube was used to keep pressure on the gold seal. In order to prevent gas leakage in the permeator, sealing was performed by heating the reactor up to 1000 °C and dwelling for 6 h. Synthetic air ($N_2$:$O_2$=4:1) was used at the feed side of dense BSCF membranes at a flow rate of 100 ml $min^{-1}$[STP] controlled by a mass flow controller (Brooks, The Netherlands). The vacuum pressure at the permeate side was regulated by a vacuum pump (MD 4 NT Vario, Vacuubrand, Germany) in the range of 5–30 mbar with a gradual increment of 5 mbar. For asymmetric membranes, the oxygen concentration in the feed gas was varied from 0.2 to 1.0 and the vacuum pressure at the permeate side was kept at 150 mbar. The oxygen permeation flux was measured using a quadrupole mass spectrometer (Omnistar, Pfeiffer, Germany). The content of $N_2$ in the effluent reveals the assembly gas leakage and its concentration was detected as less than 5% of the total permeation flux. After subtracting this leakage contribution, the oxygen permeation flux $J_{O_2}$ was calculated by

$$J_{O_2}(\mathrm{ml/cm^2\ min}) = \frac{F(\mathrm{ml\ /min})\, C_{O_2}(\mathrm{vol\%})}{A(\mathrm{cm^2})} \tag{1}$$

where $C_{O_2}$ is the concentration of the permeate oxygen, $F$ the flow rate of the sweep gas, and $A$ the effective membrane area.

### 2.3. Long-term permeation measurement

The sintered membrane for long-term measurement was mounted in the permeator and then the assembly unit was fixed in a tubular furnace. The operation temperature in the furnace was controlled by a micro-processor temperature controller to keep within ±1 °C of the set points. In the meantime, a K-type thermoelement was inserted beside the membrane in the recipient to measure the furnace temperature. The flow rate of the inlet gas (syn. air) at the feed side of the BSCF membrane was kept constant at 120 ml $min^{-1}$ [STP] and pure helium was fed to the sweep side of the permeator at a rate of 40 ml $min^{-1}$ [STP]. In contrast to the vacuum measurements, the effluent gas during operation was gathered in a gas mouse connected to the permeate side of the membrane permeator. The gas composition in the effluent was detected every 24 h by removing the shut-off gas mouse from the reactor and reconnecting it to a gas chromatograph (7890A GC, Agilent Technologies, USA). The leaked $O_2$ concentration related to the $N_2$ trace detected in the permeation flux was subtracted and the oxygen permeation flux of the membrane was calculated using Eq. (1). Membranes after long-term measurement were directly examined by X-ray diffraction (XRD) using Cu Kα radiation (D8 Advance Series 2, Bruker AXS, Germany). The microstructures of the membranes were characterized by scanning electron microscopy (SEM, Supra VP, Carl Zeiss NTS GmbH, Germany) equipped with an energy dispersive X-ray (EDX) attachment (Si(Li)-Detector, Oxford Instruments, UK) to identify the elemental composition of formed phases.

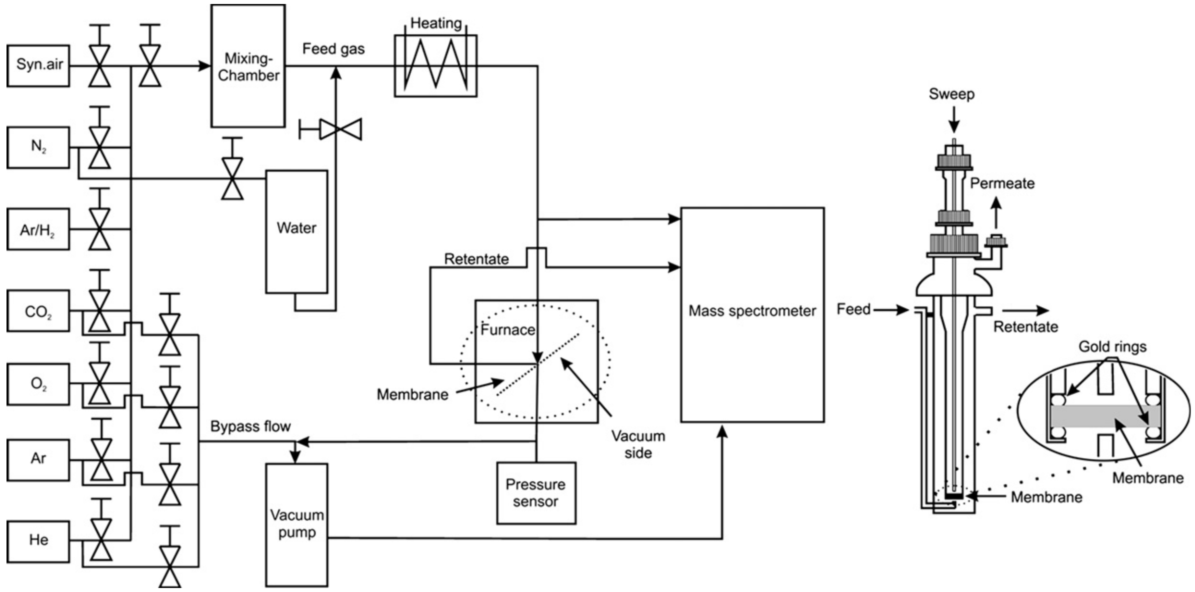

**Fig. 1.** Schematic diagram of the assembly of the membrane permeator.