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Production of pure oxygen from BSCF hollow fiber membranes using steam sweep

Adrian Leo [a], Shaomin Liu [b], João C. Diniz da Costa [a,*]

[a] FIMLab – Films and Inorganic Membrane Laboratory, School of Chemical Engineering, The University of Queensland, Brisbane, Qld 4072, Australia
[b] School of Engineering, Curtin University of Technology, Perth, Australia

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ABSTRACT

In this work, BSCF hollow fiber membranes made from a phase inversion/sintering technique produced high purity oxygen (>99.5%) at high flow rate of 9.52 ml min^{-1} cm^{-2} at 950 °C using a steam sweep gas. Long term exposure to steam sweep gas revealed loss of performance. For instance, oxygen flux remained stable up to 20 h, though undergoing a significant reduction afterwards. Similarly, the oxygen purity reduced after 40 h testing, though less significantly as oxygen fluxes. We found that steam leached the elements of BSCF, mainly forming an extra layer of insoluble carbonates of barium and strontium. This was attributed to the reaction of the perovskite with carboxylic acid ever present in steam. In addition, steam exposure at high temperature reduced the area of diffraction and crystallite sizes of the reflective planes of the BSCF membrane, thus indicating that the steam exposure deteriorated the crystal ordering. The membrane area exposed to steam become porous while covered with a porous layer of carbonates of barium and strontium, thus limiting the oxygen surface kinetics and explaining the oxygen flux reduction over time.

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1. Introduction

Cryogenic oxygen separation is preferentially used to supply oxygen for most large industrial plants [1]. Recently, other technologies have come into prominence, due primary to the need for smaller scale oxygen production, or to reduce the large operating costs associated with energy consumption in cryogenic processes, including pressure swing adsorption [2–4], polymeric [5] and dense ceramic [6–14] membrane. To overcome the problems of low oxygen purity in polymeric membrane technology, there has been a concerted effort from the research community to focus on dense ceramic membranes. These are generally perovskite type materials which deliver reasonable oxygen fluxes at high temperatures (>750 °C), the most studied materials being barium strontium cobalt iron (BSCF), lanthanum strontium cobalt iron (LSCF) or variations of these compositions. Perovskite membranes are known as mixed ionic electronic ceramic materials, which conduct both oxygen ions and electrons. As a result, the ionic diffusion of oxygen is prevalent throughout the membrane, resulting in pure oxygen production [15–17]. Recent developments made on the membrane manufacturing have delivered geometry flexibilities. The perovskite materials can be moulded as dense ceramic hollow fiber [10,18,19], tubular and flat plate type membranes [20,21].

When bulk diffusion is the limiting step, the oxygen flux through these perovskite membranes can be generally determined by the Wagner equation [22]. Wagner equation can be experimentally fitted and further simplified to the following equation [23–25] for general cases:

$$J_{O_2} = \frac{RT\sigma_i^o}{4F^2L}(p'^{-n}_{O_2} - p''^{-n}_{O_2}) \quad (1)$$

where J_{O_2} represents the oxygen flux; F is the Faraday's constant; L is the thickness of transport layer; σ_i^o the ionic conductivity at 1 atmosphere; p'_{O_2} and p''_{O_2} the oxygen partial pressure at the feed and permeate sides, respectively. Further assuming that the relationship of σ_i and oxygen partial pressure can be expressed by $\sigma_i = \sigma_i^o P_{O_2}^{-n}$, then the oxygen flux can be fitted to the following empirical equation (2) where α is constant and n can vary between negative and positive values depending on the controlling steps for oxygen transport through the perovskite membranes:

$$J_{O_2} = \alpha[p'^{-n}_{O_2} - p''^{-n}_{O_2}] \quad (2)$$

From the value of n in Eq. (2), the rate limiting step of the O_2 permeation can be roughly identified. For $n < 0$, bulk diffusion of the oxygen ion is the rate-limiting step, while for $n \geq 0.5$, the reaction of molecular oxygen with the membrane surfaces is the rate-controlling step. For $0 < n < 0.5$, the oxygen permeation is jointly controlled by both surface reactions and bulk diffusion.

Fig. 1 illustrates the effect of pressure on the oxygen flux of a conventional perovskite disk membrane calculated according Eq. (2)

* Corresponding author. Tel.: +61 7 3365 6960; fax: +61 7 3365 4199.
E-mail address: j.dacosta@uq.edu.au (J.C. Diniz da Costa).

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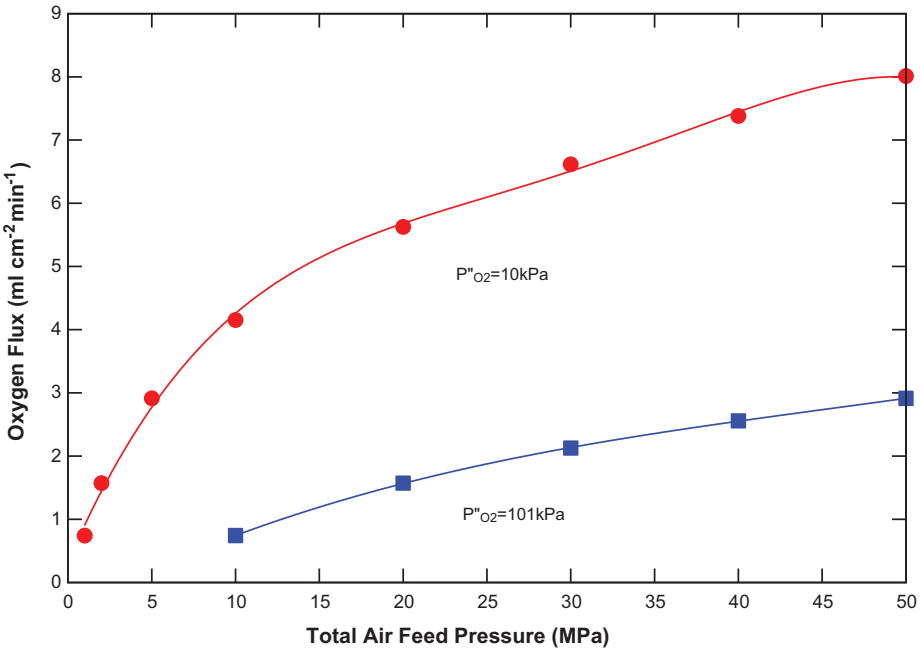

Fig. 1. Oxygen fluxes for permeate streams at oxygen partial pressures of 10 and 101 kPa.

and using $n = 1/4$ as reported elsewhere [24,25]. This case assumes a perovskite disc membrane delivering 0.74 ml cm^{-2} min^{-1} at 900 °C, with a total air feed pressure at 1 MPa, equivalent to p'_{O_2} of 0.21 MPa, and p''_{O_2} 0.1 MPa (or 101 kPa – atmospheric pressure). By keeping the permeate pressure at 101 kPa, the oxygen flux will increase by a factor of 3, if the air feed pressure is raised 5 times, from 1 to 5 MPa. This means that any benefit by increasing the oxygen flux is negated by an additional pressure requirement, leading to a high rate of energy consumption. On the other hand, if the permeate stream is kept at very low oxygen concentration (p''_{O_2} of 10 kPa), then higher oxygen fluxes can be achieved. Of particular attention, the oxygen flux at air feed pressure at 0.1 MPa is the same as for the membrane operating at and p'_{O_2} 1 MPa and p''_{O_2} 0.1 MPa. In this case, keeping the oxygen permeate pressure as low as possible greatly reduces the operating pressure by a factor of 10 or more, while the air compression requirement is no longer needed.

There are several conventional approaches to increase oxygen fluxes in perovskite membranes. This include reducing the thickness (<500 μm) of the membranes as in hollow fibers to reduce bulk diffusion limitations [26–29], compositional changes of ceramic compounds [30,31], incorporating catalysts on the surface to overcome surface kinetic limitations [32–34], and acid surface etching to further reduce the membrane thickness [35]. Though the oxygen flux increase of membranes is viewed positively, it does not address process systems associated with the pressure effect.

Another approach to increase oxygen flux is to reduce the oxygen concentration in the permeate stream by using a sweep gas. However, this approach defeats the purpose of commercial air separation, as oxygen mixed with a sweep gas would require further downstream separation, adding extra unnecessary capital and operating costs [36]. One potential variant here would be when the sweep gas would also have a beneficial application such as in oxy-fuel coal combustion. In this process, it is necessary for the oxygen to be mixed with the produced recycled CO_2 in order to control the combustion temperature. Engels et al. [37] investigated the process advantages of coupling an oxygen transport membrane with a flue gas stream, as the recycled CO_2 could be used as sweep gas in this case. Although this approach makes sense in terms of process systems, in reality perovskites are bound to react with CO_2 at high temperatures, forming carbonates [38,39]. Other method proposed include the employment of a vacuum pump in the permeate stream for the production of almost pure oxygen (97.15%) using a LSCF hollow fiber membranes [40]. Vacuum pumps are conventionally used in pressure swing adsorption units for the production of oxygen, though at much lower temperatures, and could be adapted to be employed in conjunction with membrane systems.

In this work we investigate another approach namely: producing oxygen by using a steam sweep gas. Steam can be easily generated and condensed using conventional engineering units, which facilitates the production of pure oxygen without adding major capital costs in air separation units [41]. To gauge the usefulness of this method for producing oxygen, we evaluated the long term effect of perovskite (BSCF) hollow fibers at temperatures up to 950 °C at varying steam sweep flow rates. The membranes were fully characterised using XRD, EDX, FTIR and SEM prior and after steam exposure testing in order to provide more insights into the effect of steam exposure.

2. Experimental

2.1. Preparation methods an characterisation

BSCF hollow fibers membranes were prepared by a phase inversion/sintering technique described elsewhere [15] though modified by incorporating a sulphur free binder [42]. Briefly, the BSCF powders were prepared using a combined EDTA–citrate complexation method, and nitrates of barium, strontium, cobalt and iron with purity greater than 99.9% (Sigma–Aldridge). The prepared BSCF powders were calcined in air at 500 °C for 4 h, and milled to obtain fine particles of less than 3 μm size. The BSCF powder was added to a mixture of 1-methyl-2-pyrrolidinone (NMP) (Synthesis grade, Sigma) and a sulphur free binder polyetherimide (PEI) (SABIC Innovative Plastics) using a mass ratio 6:1:5 and stirred for 24 h to ensure a uniform mixture. Amounts of 0.5–1% by mass polyvinyl pyrrolidinone (PVP) (Sigma) were added to adjust the viscosity of the mixture. To form the BSCF–NMP–PEI mixture into the required hollow fiber geometry, a tube-in-orifice spinneret with orifice diameter/inner diameter of 2.5 mm/0.8 mm was used. Tap

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