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Highly stable $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ hollow fibre membrane for air separation swept by steam or steam mixture

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ABSTRACT

Perovskite oxide ceramic membranes have the potentials for industrial oxygen production, particularly to replace the conventional expensive air separation units, which is of significance to improve the viability of the clean energy technologies like IGCC and Oxyfuel projects. In most of these applications, the steam presence is unavoidable thus requiring these membranes to be stable in the steam-containing atmosphere under high temperatures. In this work, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\alpha}$ (LSCF) perovskite hollow fibre membrane was prepared and tested for O_2 separation in the presence of steam in the sweep gas. Three membranes were successfully tested at temperature of 900 °C using the sweep containing 3%, 4–12% and 100% steam (balanced by helium) for 370, 200 and 500 h, respectively. In the long run, the steam can etch the membrane surface, as evidenced by the leaching of iron and the formation of strontium carbonate. This etching process however is too slow to cause substantial damage on the membrane performance. Using pure steam sweep, the LSCF membrane was operated at 900 °C for nearly 500 h without any sign of O_2 flux decay, compared favourably with $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\alpha}$ (BSCF) hollow fibre membranes, which only lasted for 90 h. In contrast to the severe poisoning effects of other acid gases like SO_2 or NO_x on the O_2 permeation through similar LSCF membrane, the detrimental effect of steam is negligible. In fact, the presence of minor steam less than 12% in the sweep is kinetically favourable for the surface oxygen exchange reactions, leading to the improvement of the O_2 flux.

1. Introduction

Oxygen is the second-largest (by volume) industrial gas produced from air separation with annual global production capacity reaching hundreds of millions of tons [1]. This market is rapidly expanding by the ever-increasing demand from industries like steel/aluminium manufacturing, chemical plants, and from clean energy applications like Integrated Gasification Combined Cycle (IGCC) or Oxyfuel projects [2]. Currently, industrial O_2 is produced through the cryogenic distillation by cooling down the air to −185 °C. Thus, resultant high capital/operation cost largely restricts its application in clean energy deployment. To reduce the cost, membrane separation technology via mixed ionic and electronic conducting (MIEC) ceramics has been developed [3–5]. The attractiveness of this ceramic membrane technology has been demonstrated by Air Products with their investment of $148 million since 1990s [6]. The fundamental studies of these MIEC membranes were started in 1980s with the pioneering work from Teraoka and co-workers [7]. Unlike microporous membrane where the separation performance is determined by the gas molecular diameter, membrane pore size and gas adsorption properties, O_2 transport through MIEC ceramic membranes occurs via surface reactions and ionic/electronic diffusion [4,8,9]. These ceramics allow simultaneous conduction of oxygen ions and electrons at elevated temperatures (> 800 °C), the so-called mixed ionic and electronic conductivity. So far, a series of perovskite ceramics with different compositions have been explored surrounding the general formula of $ABO_{3-\delta}$ where A and B sites can be individually or jointly occupied by different metal elements [3,10–23]. A trade-off generally exists between the O_2 flux and material stability. Membranes with high O_2 fluxes with one typical example of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) often have poor chemical stability in real application conditions involving low oxygen partial pressure atmosphere and in the presence of poisoning gases like CO_2, H_2S, H_2O, SO_2 and CH_4 [24,25]. These poisoning gases readily react

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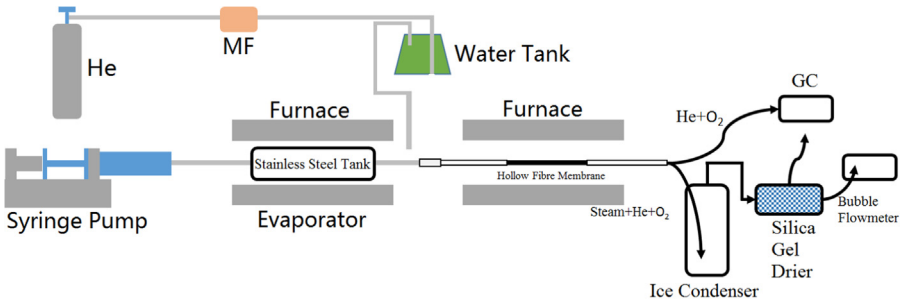

Fig. 1. Schematic of oxygen production using LSCF hollow fibre membrane.

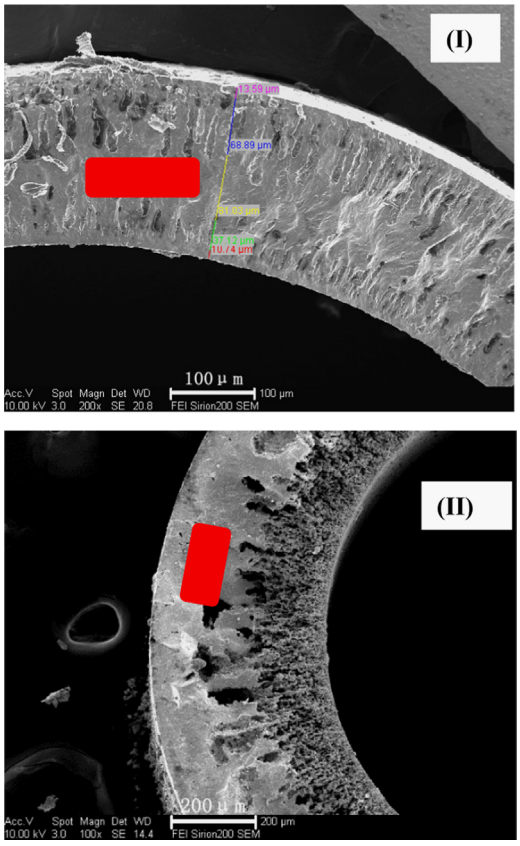

Fig. 2. Cross-sectional SEM images of two typical LSCF hollow fibre membranes spun using H_2O as the internal and external coagulants. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

with the metal oxides in the perovskite structure leading to the membrane deterioration. Relatively speaking, material stability is more important as the O_2 flux of the robust membrane can be improved through engineering approaches such as thin film technology. With sufficient stability, the membrane applications can be extended from pure O_2 production solely under mild conditions to membrane reactors for chemical synthesis at severe conditions comprising a simultaneous gas separation and reactions [26]. Another envisaged application is to produce a mixture of O_2 and CO_2 and utilise power plant flue gas (CO_2) as the sweep gas for combustion in the current boiler system, which cannot tolerate the high flame temperature from pure oxygen combustion [27]. This strategy in turn favours the viability of Oxyfuel project as a cheaper alternative relative to the production of pure oxygen. Previously, our group demonstrated a proof-of-concept perovskite membrane module consisting of 899 $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\alpha}$ (LSCF) hollow fibres that could be operated for more than 1000 h and providing 3 L min^{-1} O_2 flow rate with the purity of at least 99% [29]. The effects of CO_2 or SO_2 presence in the sweep gas on the membrane performance were also well-documented elsewhere [25,28,30].

In this work, we examined the effects of steam in the sweep gas on the LSCF hollow fibre membrane performance. Initially, 3–12% of steam in helium (He)-dominated sweep gas was chosen to check the possible decay of O_2 flux and the membrane deteriorations. Subsequently, we tested the feasibility of using pure steam to replace He (as sweep gas) since pure steam can be easily generated and separated by a simple condensation process [31,32]. LSCF membrane could operate for more than 500 h without any apparent performance decay while BSCF membrane deteriorated in less than 25 h [32].

2. Experimental section

2.1. Fabrication and characterisation of LSCF hollow fibre membranes

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\alpha}$ (LSCF) perovskite powders for spinning hollow fibre membranes were prepared through a sol–gel process as detailed elsewhere [25]. The powder precursor was calcined at 800 °C for 4 h to remove the residual carbon and to form the desired structure, ball-milled for 48 h in an agate jar and sieved through a sifter of 200-mesh or 24 μm sieve-pore diameter. LSCF hollow fibre membranes were prepared by the phase-inversion/sintering technique. The detailed procedures of the method were described elsewhere [25]. In this work, the starting mixture for spinning consisted of 65.51 wt% LSCF powders, 6.90 wt% polyethersulfone (PESf) and 27.59 wt% 1-methyl-2-pyrrolidone (NMP). Water was used as the internal and external coagulants. A spinneret with the orifice diameter/inner diameter of 3.0/1.2 mm was used to extrude the hollow fibre precursor at room temperature. Deionised water and tap water were used as the internal and external coagulants, respectively. Sintering was carried out at 1350 °C for 4 h to obtain gas-tight hollow fibre membranes. The membranes were characterised using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD).

2.2. O_2 permeation measurement

O_2 permeation experiments were conducted using the apparatus schematically shown in Fig. 1 LSCF fibres of 50 mm-length were suspended in a tube furnace with outside surface exposing to air atmosphere. Quartz tubes were attached to both ends of the LSCF fibres and sealed by a silver-based sealant. Permeation experiments were conducted by passing a sweep gas through the lumen side of the hollow fibre and varying the furnace temperature between 850 and 950 °C. Six different gas streams - pure helium, 3%, 4%, 7%, 12% steam in helium and pure steam were used as a sweep gas. He flow rate was adjusted with the mass flow