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Pilot-scale production of oxygen from air using perovskite hollow fibre membranes

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ABSTRACT

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\alpha}$ (LSCF) hollow fibre membranes prepared by a phase-inversion/sintering technique were assembled into a membrane system to produce oxygen of high purity (>99%) from air at elevated temperatures. The separation performances, stability, scaling-up effect and the energy consumption of the membrane system were investigated both theoretically and experimentally. The membrane system containing 889 hollow fibres could yield maximum 3.1 L(STP) min^{-1} oxygen with the purity of 99.9% at 1070 °C and 98.5 kPa vacuum degree, but the temperature higher than 1070 °C would lead to the system failure. It showed the potential of much higher production rates only if the high-temperature sealing problem could be solved. When operated at around 960 °C, the system exhibited more than 1167 h longevity with the oxygen production rate of 0.84 L(STP) min^{-1} and oxygen purity of 99.4%. The energy consumption of the system increased with operating temperature but the energy consumption per unit oxygen product decreased with increasing the operating temperature and the effective membrane areas. In order to reduce the oxygen cost to commercial level, heat exchangers have to be integrated in the membrane system to recover the heat energy in both the exhaust gas and the oxygen product. The oxygen recovery should be limited within 20–40% for the sake of both energy and membrane area savings.

1. Introduction

Oxygen production from air is of great importance in both environmental and chemical industries. It is usually achieved by cryogenic distillation, pressure swing adsorption (PSA) or by polymeric membrane separation. These processes are either of high energy consumption or unable to produce oxygen of high purity. Alternately, dense mixed conducting membranes such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\alpha}$ (LSCF) perovskite which exhibit appreciable oxygen ionic and electronic conductivity have become of great interest as a potentially economical, clean and efficient means of high pure oxygen production [1–7]. When an oxygen partial pressure gradient is imposed across such dense membranes at a high temperature (usually >700 °C), the oxygen may be transferred from the high partial pressure side to the low partial pressure side without the need of electrodes and external electrical loadings, making the membrane system and operation much simplified.

In recent years, perovskite hollow fibre membranes have been successfully prepared by a phase-inversion/sintering process [8–12]. Such hollow fibre membranes can provide much larger areas per unit volume than other configurations such as flat sheet or tubular, thus it is possible to reduce the membrane system size remarkably. Furthermore, the hollow fibre configuration also makes the high-temperature sealing less problematic in fabricating membrane modules [13–15]. In this work, we developed a perovskite hollow fibre membrane system that could produce over 3 L(STP) min^{-1} oxygen gas with the purity of >99%. The separation performances, the stability, the scaling-up effect and the energy consumption of the perovskite membrane systems have been investigated both theoretically and experimentally.

2. Experimental

2.1. LSCF powder and hollow fibre membranes

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\alpha}$ (LSCF) hollow fibre membranes were prepared by a phase-inversion/sintering technique using the powders synthesized through a sol–gel combustion process which were described elsewhere [8,12]. The resultant hollow fibre membranes were usually *ca.* 28–32 cm in length and around 0.12/0.18 cm in i.d./o.d. One end of the hollow fibres was closed with the same LSCF material and the gas-tight property was achieved after sin-

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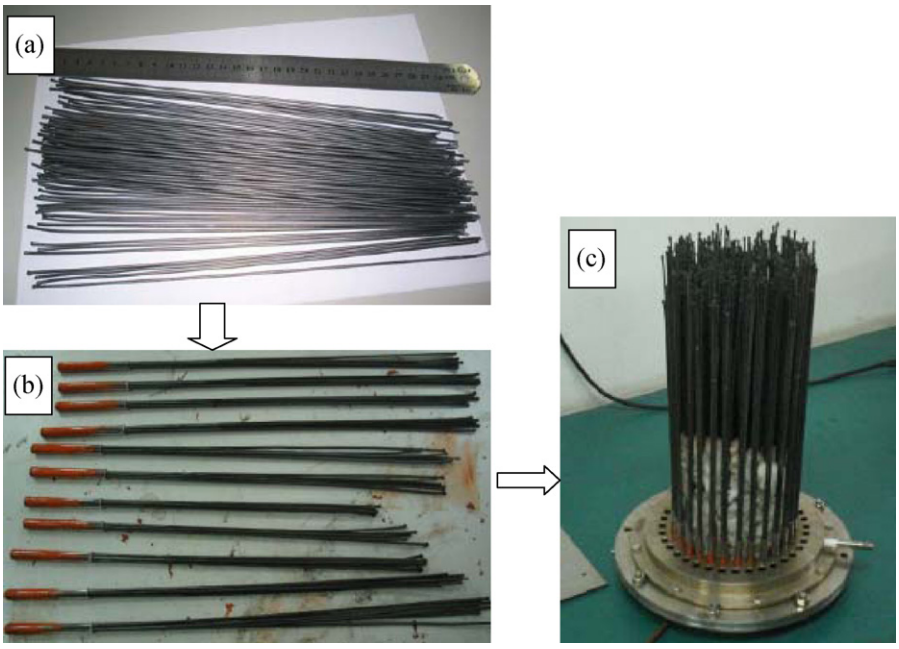

Fig. 1. Photos of (a) the LSCF hollow fibre membranes; (b) the hollow fibre bundles; and (c) the hollow fibre membrane module.

tering. Surface modification was conducted on the hollow fibres by coating catalysts on the outer surface so as to improve the permeation flux of the hollow fibre membranes. The catalyst consisted of a perovskite with high Co content and an Ag paste with the particle size <7 μm and was mixed in weight ratio of 6:1. The detailed coating procedures were described elsewhere [16].

2.2. Hollow fibre membrane module and system

In practical applications, the hollow fibres must be assembled into a membrane module. For the sake of sealing and facile replacement of broken fibres, we first bundled 7 fibres together in a quartz tube (8 mm in diameter and 70 mm in length) with a high-temperature silicone sealant (1592, purchased from Tonsan New Materials and Technol. Co., Beijing) that is able to withstand up to 350 °C. The fibre bundles as required were then placed in a stainless steel holder. Fig. 1 shows the LSCF hollow fibre membranes, the fibre bundles and the membrane module. It is very important to avoid any leakage in order to obtain highly pure oxygen product. Therefore, each hollow fibre was individually tested to be gas-tight prior to bundling and every bundle was again tested to be free of leakage before integrating them into a module. In this work, three modules containing 1 bundle (7-fibre module), 9 bundles (63-fibre module) and 129 bundles (889-fibre module) respectively were fabricated to study the scaling-up effect. The effective membrane areas by subtracting the sealing length from the whole fibre length for these modules were *ca.* 78 cm^2, 702 cm^2 and 9914 cm^2, respectively.

The hollow fibre membrane system for oxygen production is schematically shown in Fig. 2. The hollow fibre membrane module was placed under a vertically positioned tubular furnace. An insulator was placed between the bottom inlet of furnace and the stainless steel holder so that the temperature at the sealing points was lower than that the sealant can withstand. A vacuum was applied to the membrane module using a claw rotor oil-free vacuum pump (2ZBL, purchased from Beijing Huaxiajia Sci & Tech Inc.). The operating vacuum degree was controlled using a frequency modulator (Suny3200, from Sunye Electric Co.) fitted to the vacuum pump and was measured with a digital pressure sensor (PSA, from Autonics Co.). The oxygen concentration and the flow rate of the product were measured using an oxygen analyzer (TG-J310, from Xi'an Taige analysis instrument Inc.) and a digital film flow meter (SF-1U/2U, purchased from Horiba Stec Co. Ltd.), respectively. The operating temperature was controlled using a temperature controller with a K-type thermocouple positioned in the middle of the furnace. Meanwhile, a temperature gauge fitted with another K-type thermocouple was used to monitor the temperature at the sealing points. In the operation, the oxygen product flow rate and the concentration of the oxygen product were recorded with time

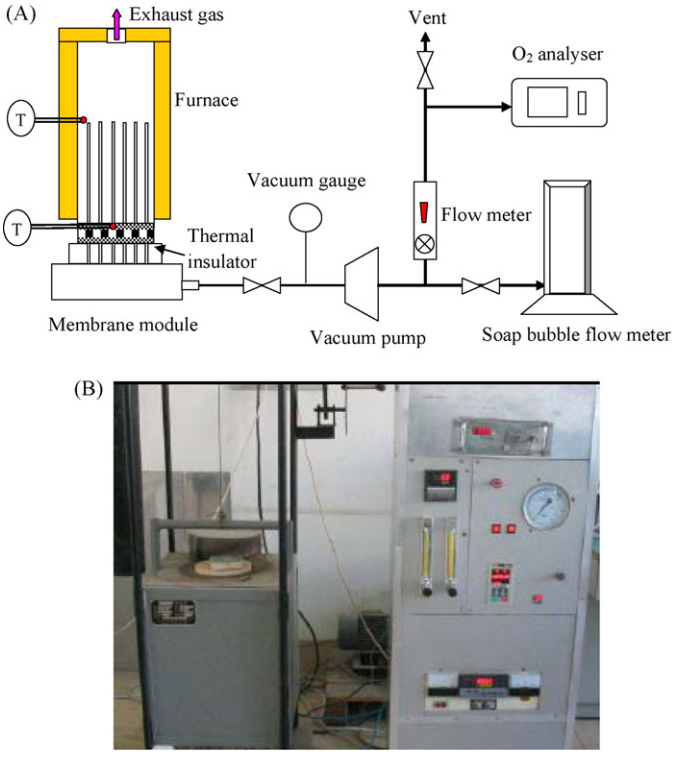

Fig. 2. Hollow fibre membrane system for oxygen production (A) flow chart; and (B) photo of the setup.