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Synthesis, Characterization and Oxygen Permeability of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ Membrane and Coating on Dense Substrate

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Abstract: A porous $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF6428) layer coated on the dense substrate, made from the same material has been prepared. The first part of the study focused on the development of dense LSCF6428 substrate with gas tight properties by controlling the sintering conditions. To further improve the performance of LSCF6428 perovskite membrane, an effort was made on surface modification by coating a porous LSCF6428 layer on dense membrane surface. The characterization of the thermal stability (TGA), phase structure (XRD), morphology (SEM) and oxygen desorption properties (O_2 -TPD) were investigated. The cross-sectional images of the surface modified membrane system indicated that the porous LSCF6428 layer had uniform thickness and showed excellent adhesion to the dense substrate. The oxygen flux of the surface modified membrane was improved by 30-60% with the maximum flux obtained was $0.86 \text{ mL cm}^{-2} \text{ min}$ at 800°C .

Key words: $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, surface modification, characterization, oxygen permeation

INTRODUCTION

Membrane gas separation based on dense ceramic membranes made from Mixed Ionic-Electronic Conducting (MIEC) oxides have recently attracted significant attention from both research community and industrial sectors due to their potential applications in air separation for oxygen production (Ge *et al.*, 2009; Li *et al.*, 2010; Park *et al.*, 2009; Sunarso *et al.*, 2010). This newly emerged technology is generally recognized as an economically promising technique with a great potential to reduce the oxygen production cost by 30% compared to the conventional methods (Smart *et al.*, 2010). Considering the high oxygen permeability and good chemical stability among lanthanum cobaltite materials (Li *et al.*, 1999; Zeng *et al.*, 2007; Jin *et al.*, 2001; Jin *et al.*, 2000), perovskite-type $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF6428) was selected as a promising mixed conducting ceramic membrane material for application in oxygen separation from air. A major challenge for large-scale technical applications is to increase the oxygen flux through these membranes and/or to reduce operating temperatures. The modification of the membrane surface is a smart breakthrough to increase the oxygen permeation performance when the flux is determined by the oxygen exchange reaction (Sunarso *et al.*, 2008). Moreover, higher surface/volume ratios can be achieved in a porous top coating by promoting the formation of a mesoporous pore system (Kusaba *et al.*, 2006).

MATERIALS AND METHODS

Synthesis of LSCF6428 membrane: Commercially available LSCF6428 powders with surface area of $6.3 \text{ m}^2 \text{ g}^{-1}$ and $d_{50} = 0.32 \text{ m}$ (purchased from Fuel Cell Materials, Lewis Center, OH) was used as the membrane material since the conventional powder synthesis process is time consuming. Weighed amount of LSCF6428 powder was put into a stainless steel mold of 20 mm diameter and uniaxially pressed with a pressure of approximately 5 Ton for several min. The green disk was sintered at 1200°C for 5 h in air at heating/cooling rate of 1°C min^{-1} . The sintered membrane has a diameter of 16 mm and thickness of 1.0 mm. For surface modification, the porous LSCF6428 layer was coated on the sintered membrane surface. For the preparation of the coating slurry, the LSCF6428 powder was dispersed in proper amount of isopropanol, ethylene glycol and glycerol (Chen *et al.*, 2009). The slurry mixture was stirred constantly for 1 h. Subsequently, the perfectly mixed slurry was directly deposited on the membrane surface using settlement method (Matsuka *et al.*, 2010) and was left until the powder was fully settled. The surface modified membrane was dried at 100°C for 60 min followed by calcination at 1100°C for 5 h with a heating/cooling rate of 1°C min^{-1} to burn out the organic materials and generate the porous LSCF6428 layer on the membrane surface.

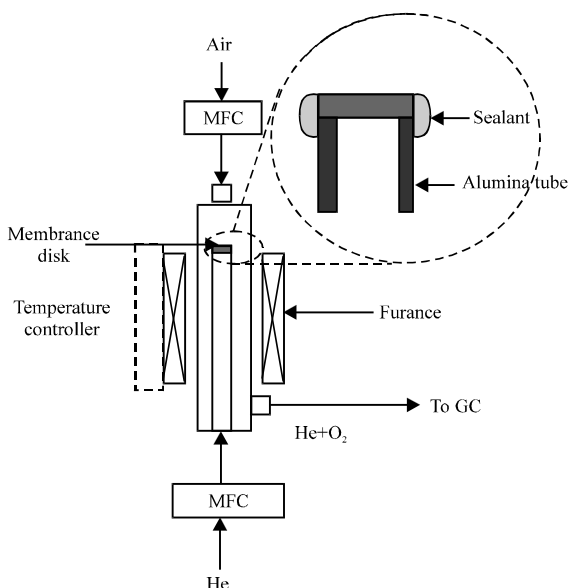


Fig. 1: Schematic of apparatus for the oxygen permeation measurement

Characterization: The properties of the LSCF6428 powder was determined by thermogravimetric analysis (Mettler-Toledo) and O_2 -TPD experiment (Micromeritics AutoChem II-2920) while the crystal phases of the sintered membrane was determined by X-ray diffraction analysis (BRUKER D8 ADVANCE, Germany using $Cu K\alpha$ radiation). A gas-tight test was also conducted on the sintered membrane using helium at room temperature. The morphological features of the membrane before and after surface modification were examined by scanning electron microscopy (SEM) (Zeiss Supra 35VP).

Oxygen permeation measurement: The oxygen permeation fluxes were measured using the apparatus shown in Fig. 1. High temperature ceramic sealant (Sauereisen) was used as the sealant to seal the disk onto the dense alumina tube. Air was introduced into the upstream of the membrane and helium as the sweep gas for the permeating oxygen was fed to the downstream of the membrane. Both upstream and downstream were maintained at the atmospheric pressure. The effluent streams were analyzed by gas chromatography (Agilent 6890) equipped with a 3 m 5 A molecular sieve column operated at $80^\circ C$, with helium as the carrier gas. The oxygen permeation flow through the membrane was calculated from the flow rates and the oxygen concentrations in the effluents. The amount of nitrogen leakage through the pores or cracks of the sealing part will be considered when measuring the oxygen flux. It can be assumed that the nitrogen leaking is in agreement with the Knudsen diffusion mechanism and the correlation of the

fluxes of leaked nitrogen and oxygen is expressed by Shao *et al.* (2001):

$$J_{O_2}^{leak} : J_{N_2}^{leak} = \sqrt{\frac{32}{28}} \times 0.79 : 0.21 \quad (1)$$

The oxygen permeation flux, J_{O_2} ($mL \cdot cm^{-2} \cdot min^{-1}$) will be calculated from the flow rate of the elute from the downstream, F ($mL \cdot min^{-1}$) and oxygen concentration of the exit gas, C_{O_2} (%) and the effective area of the membrane, S (cm^2) based on the equation below:

$$J_{O_2} = \frac{F \times C_{O_2}}{S} \quad (2)$$

By introducing the Eq. 1 into the Eq. 2, the oxygen permeation flux can be expressed as:

$$J_{O_2} = \left(C_{O_2} - C_{N_2} \times \frac{0.21}{0.79} \times \left(\frac{28}{32} \right)^2 \right) \times \frac{F}{S} \quad (3)$$

where, C_{O_2} (%) and C_{N_2} (%) are the concentration of oxygen and nitrogen measured in the gas on the sweep side, respectively.

RESULTS AND DISCUSSION

Oxygen temperature programmed desorption (O_2 -TPD):

The O_2 -TPD profile of the LSCF6428 oxides is shown in Fig. 2. Two O_2 desorption peaks were observed: one was between 350 and $450^\circ C$ (peak α) and the other one was between 700 and $900^\circ C$ (peak β). It has been suggested that the nature of peaks α and β were associated with oxygen permeability and structural stability, respectively (Tong *et al.*, 2003). The first α peak in the low temperature zone was correlated to the reduction of Co^{4+} to Co^{3+} and Fe^{4+} to Fe^{3+} while the second β peak in the high temperature zone was correlated to the reduction of Co^{3+} to Co^{2+} . Based on the O_2 -TPD profile, it can be concluded that the LSCF6428 material has both good oxygen permeability and structural stability properties.

Thermogravimetric and differential thermal analysis (TG-DTA):

The TG-DTA profile of the LSCF6428 oxides recorded in nitrogen (99.999%) is shown in Fig. 3. It can be seen from Fig. 3 that the weight of the LSCF6428 sample decreased slowly with the increase of the temperature. However, the TGA result showed a sharp decrease of the weight of the LSCF6428 oxides at temperatures between 700 and $900^\circ C$ which was in good agreement with O_2 -TPD profile. The temperature dependent weight loss could be attributed to the release of oxygen from the lattice structure. From Fig. 3, the DTA

profile of LSCF6428 oxides showed no endothermic or exothermic peak in the whole heating process indicating that no structure transition occurred for the ceramic oxide of LSCF6428 (Tong *et al.*, 2003). Conclusively, the TG-DTA results showed that it was possible to synthesis membrane from LSCF6428 material at sintering temperature higher than 1000°C.

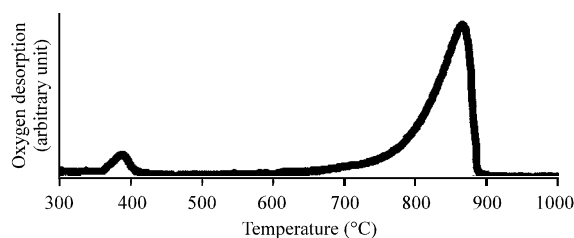


Fig. 2: O₂-TPD profile of LSCF6428 oxides

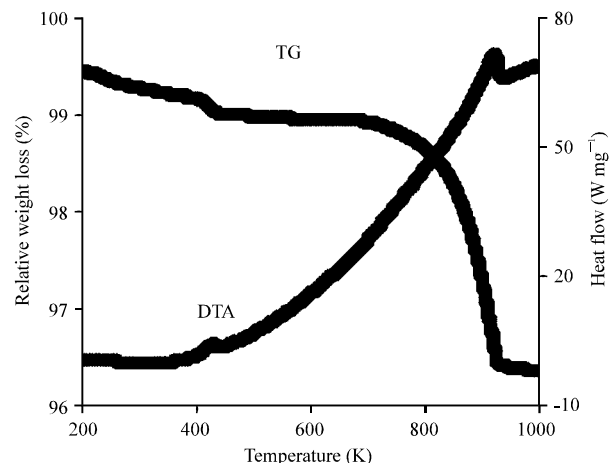


Fig. 3: TG-DTA curve of LSCF6428 oxides

X-ray diffraction (XRD): As shown in Fig. 4, the main peaks in the XRD patterns of the dense membrane sintered at 1300°C for 5 h shifted to the left for certain degrees as compared to the original LSCF6428 powder patterns. The shift could be attributed to the tilt of crystal lattice caused by the big ionic radius and excessive content of La at A site (Tan *et al.*, 2003). The intensity of the corresponding characteristic peak of the main perovskite peaks of the sintered LSCF6428 membrane was slightly higher than the original LSCF6428 powder which suggested that the crystals in the dense LSCF6428 membrane have become larger due to the high-temperature sintering and appropriate dwelling time.

Scanning electron microscopy (SEM): Figure 5 shows that the surface of unmodified LSCF6428 dense membrane was quite smooth and the grain boundary of LSCF6428 particles could not be distinguished. It is worthwhile noting that the membrane was not 100% densified as there

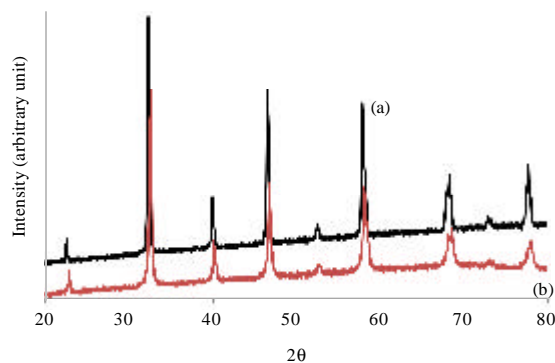


Fig. 4: XRD patterns of (a) LSCF6428 powder and (b) dense LSCF6428 membrane calcined at 1200°C

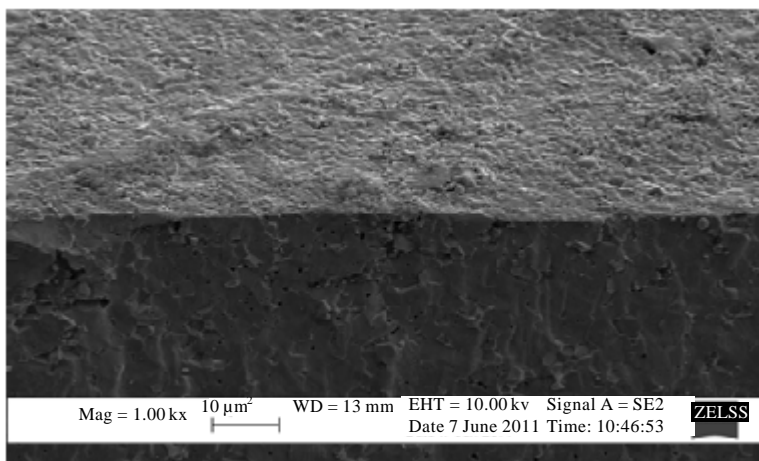


Fig. 5: SEM micrograph of the non-modified membrane

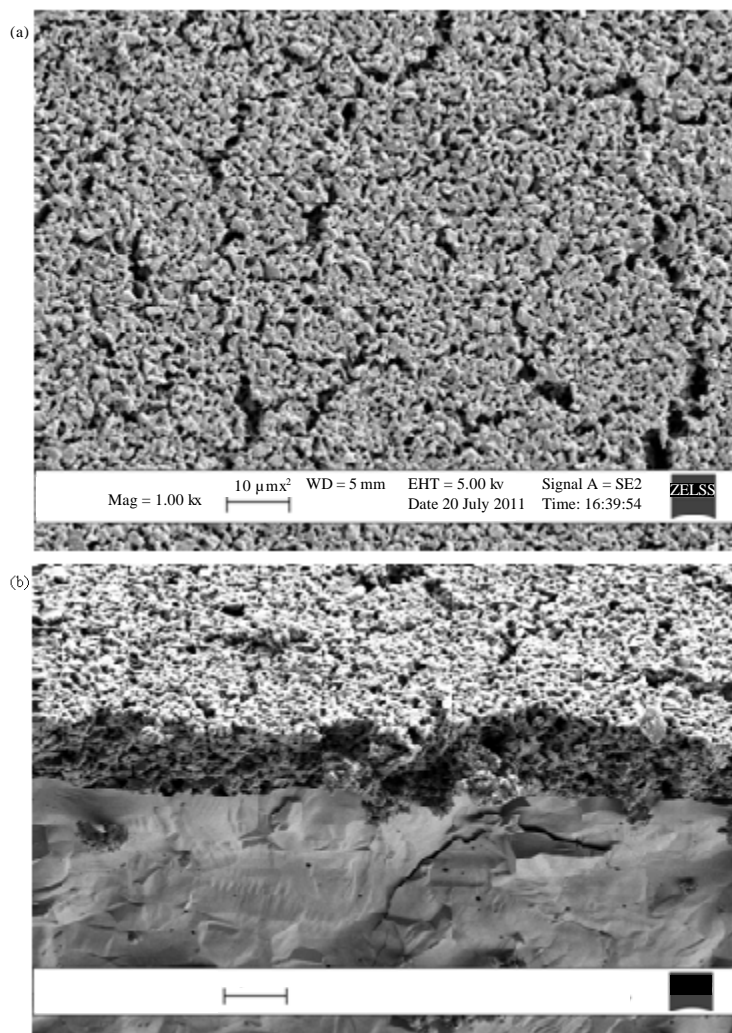


Fig. 6(a-b): SEM micrographs of the surface modified membrane (a) Surface and (b) Cross-section

were still many isolated pores along the cross-section area; however, there was no connected porosity across the membrane. The gas-tightness test conducted showed that the membrane was leak-tight to helium up to the pressure of 1.0 MPa indicating that the gas-tightness of the membrane prepared was enough to endure the environment for oxygen permeation. The SEM micrograph of the top layer of the surface modified membrane which is shown in Fig. 6a demonstrated that the layer was porous. It can also be observed that the porous LSCF6428 layer with thickness of 10 μm integrated well to the membrane surface, as shown in Fig. 6b.

Oxygen permeation: The effect of temperature on oxygen permeation flux was investigated from 600-800°C by

introducing 200 mL min⁻¹ air as feed gas ($P_{\text{H}} = 0.21 \text{ atm}$) and 100 mL min⁻¹ helium as sweep gas ($P_{\text{I}} = 10^{-5} \text{ atm}$) separately in the two sides of the membranes. Figure 7 shows the oxygen permeation flux was increased in almost linear trend as temperature increased irrespective of membrane modification indicating the improved flux was due to the enhancement of oxygen diffusion and surface reaction rate at high temperatures. The oxygen permeation flux of the modified membrane was higher than that for the unmodified membrane by 30-60%. For example, the oxygen fluxes through unmodified membrane was increased by 0.22 mL cm⁻² min⁻¹ from 0.34 (600°C) to 0.56 mL cm⁻² min⁻¹ (800°C) through modified membrane by 0.33 mL cm⁻² min⁻¹ from 0.53 (600°C) to 0.86 mL cm⁻² min⁻¹ (800°C). It is worthwhile noting that

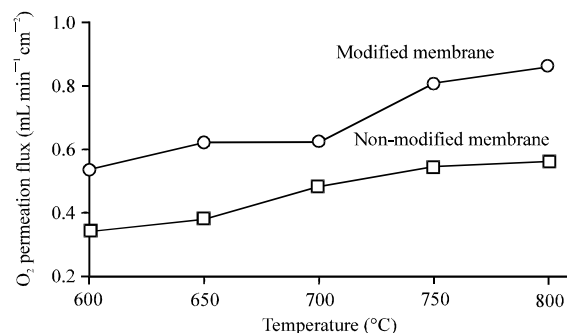


Fig. 7: Oxygen permeation flux of LSCF6428 according to surface modification (unmodified and modified membrane)

the surface reactions between molecular oxygen, lattice oxygen, oxygen vacancies and electron-holes play a crucial role in the determination of oxygen permeation rate for a membrane with thickness less than 1.1 mm (Chen *et al.*, 2009). In this case, the oxygen permeation flux of modified membrane was higher than of non-modified LSCF6428 dense membrane due to improved reaction kinetics. It was also observed from the experimental result that the surface reaction was dominant probably in high temperature region.

CONCLUSIONS

A dense perovskite type ceramic oxide LSCF6428, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ with gas tight properties has been prepared by controlling the sintering conditions. In order to improve the performance of LSCF6428 perovskite membrane, a porous layer made from the same material was coated on the dense substrate by settlement method followed by sintering at 1100°C for 5 h. The resulted surface modified LSCF6428 membrane not only exhibited uniform thickness of porous LSCF6428 layer and excellent adhesion to the dense substrate but also possessed higher oxygen permeation flux than that of unmodified LSCF6428 membrane. The oxygen flux of the surface modified membrane was improved by 30-60% with the maximum flux obtained was $0.86 \text{ mL cm}^{-2} \text{ min}^{-1}$ at 800°C.

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