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Feasibility Study of LSCF5582 Membrane Integration into a Nitrogen based Chemical Looping Air Separation Process

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Graphical abstract

Highlights

- LSCF5582 membrane characterisation for integration into N_2 -CLAS is performed.
- Enhanced O_2 separation is achieved for membranes sintered at 1200-1225 °C.
- Maximum O_2 permeation flux is obtained at sintering temperature of 1200 °C.
- Under reducing environment of N_2 , LSCF5582 sintered at 1225 °C performed best.

Abstract

This study investigates the suitability and effectiveness of $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF5582) membrane for integration into the reduction reactor of a Nitrogen based chemical looping air separation (CLAS) process for exclusive separation of oxygen. First, the structural and chemical characteristics as well as the oxygen separation properties of LSCF5582 membranes, prepared at sintering temperatures of 1050-1350 °C, were examined to obtain the optimum range of sintering temperatures resulting in membranes with enhanced oxygen separation from air. This was achieved by determining the oxygen permeation properties of LSCF5582 membranes under the reducing environment of the Nitrogen based CLAS process, whereby oxygen is liberated from CuO oxygen carriers on the feed side of the membrane using nitrogen as a reducing gas. Membrane characterisation results showed that a single phase dense LSCF5582 membrane was formed at the sintering temperature range of 1200-1225 °C obtaining a maximum oxygen permeation flux of $0.67 \text{ ml.min}^{-1}.\text{cm}^{-2}$ and oxygen recovery of 27% at the sintering and operating temperatures of 1200 °C and 900 °C, respectively. At the same operating temperature, under the reducing environment of nitrogen, the LSCF5582 membrane sintered at 1225 °C was found to perform best achieving an oxygen permeation flux and oxygen recovery of $0.77 \text{ ml.min}^{-1}.\text{cm}^{-2}$ and 76%, respectively.

Keywords: LSCF5582 membrane; Characterisation; Sintering temperature; Oxygen generation; CuO oxygen carrier; Chemical looping.

6. Nomenclature

A	The effective membrane area (cm^2)
$\text{C}_{\text{O}_2, \text{ feed}}$	The oxygen concentration of the feed stream
$\text{C}_{\text{O}_2, \text{ permeate}}$	The oxygen concentration of the permeate stream
F	The permeate flow rate (ml.min^{-1})

F_{feed}	The flow rate of the feed stream (ml.min^{-1})
F_{Sweep}	The flow rate of the sweep gas (ml.min^{-1})
J_{O_2}	The oxygen permeation flux ($\text{ml.cm}^{-2}.\text{min}^{-1}$)
L	Membrane thickness, mm
LSCF5582	$\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membrane
M	Molar weight of oxygen atoms
M_0	Molar weight of the sample at the stoichiometric oxygen composition, $\delta = 0$
W_0	weight of the sample at the stoichiometric oxygen composition, $\delta = 0$, (mg)
$W(t)$	Sample weight at equilibrium temperature (mg)
x_{N_2}	Nitrogen mole fraction (-)
x_{O_2}	Oxygen mole fraction (-)

1. Introduction

There is a worldwide demand for oxygen in the production of chemicals, clean fuels and power. Currently the production of oxygen at industrial scales relies on cryogenic distillation and adsorption based technologies. Although these air separation technologies are mature, the high energy intensity and costs are their main drawbacks under the current economic and energy constraints. The Chemical Looping Air Separation (CLAS) process [1] developed at the University of Newcastle, Australia, for tonnage oxygen production, addresses the mentioned shortcomings by significantly reducing the energy footprint [1-5]. CLAS works in a cyclic fashion by continuous circulation of oxygen carrier (e.g., metal oxide) particles between a set of two interconnected reactors, where oxidation (O_2 coupling) and reduction (O_2 decoupling) of oxygen carrier particles take place, respectively. In the original version of the CLAS process, the reduction half cycle is carried out in the presence of steam so that the desired oxygen product can be obtained by condensing steam. However, the production and condensation of steam is energy consuming and if it can be replaced by an alternative method, the overall energy footprint of the CLAS process can be further reduced. Motivated by this, the attention was turned on to developing another variant of the CLAS named Membrane Integrated Chemical Looping Air Separation (MICLAS) where the oxygen product from the reduction reactor is

separated from another suitable reducing gas (e.g. N_2) rather than steam using an oxygen transport membrane (OTM) (Figure 1).

Integration of oxygen transport membranes into a range of different processes has been reported in literature with the main focus being in the context of oxy-fuel [6-9]. The findings of these studies indicate that for producing high purity oxygen, the membrane should be dense (94%), highly stable under harsh operating conditions (1000 °C and $0.21 - 10^{-22}$ atm), possess high mixed ionic electronic conductivity, have similar thermal expansion coefficient to the adjacent materials [10-12] and exhibit high mechanical stability. Perovskite membranes are a classification of OTMs which possess these characteristics. ABO_3 represents the chemical structure of perovskite in which A and B are cations and O is an oxygen anion. The “A” site in ABO_3 is generally occupied by a large alkali, an alkali earth and rare earth metals such as barium, lanthanum or strontium; while the “B” site is occupied by smaller rare earth metals or transition metals such as cobalt or iron. Transition metals improve the densification of the membranes, not only by forming cation vacancies, which facilitate mass transport, but also by lowering the melting temperature of the liquid phases that facilitate liquid phase sintering [13]. The A site cation is usually larger than the B site cation in a perovskite structure due to the different coordination environment [14]. The A-site and B-site dopants are added to the ABO_3 structure to enhance the densification of the membranes [13]. In order for defects or vacancies (δ) to form in the perovskite structure of ABO_3 , the dopants of A' and B' are introduced on the A and B sites to produce $A_xA'_{1-x}B_yB'_{1-y}O_{3-\delta}$. The vacancies provide a pathway for ions to migrate through the crystal structure of the perovskite where oxygen permeation flux increases at increased vacancy concentrations [14]. Perovskite membranes (e.g., LSCF compounds) possess theoretically infinite selectivity [15-17] toward oxygen because oxygen ions are the only species transferring through the vacancies of the membrane. In OTM, oxygen ions transport from the high oxygen partial pressure side to the low one, while electrons move in the opposite direction and complete the internal electric circuit. Therefore, there is no need for the external circuit or electrical power for the electron conduction in the OTMs. As ionic conductivity for the OTM is directly related to the crystal structure [18], there should be a minimum sintering temperature to form vacancies in the crystal structure of the membranes [19]. However, there is a trade-off between the concentration of oxygen vacancies and the mechanical stability of the perovskite membranes. The mechanical stability of the OTM

decreases at significantly high concentrations of oxygen vacancies (δ) due to the presence of excessive stress and the lattice expansion [20].

Sr–Co–Fe (SCF) perovskite membranes demonstrated the highest oxygen permeability among all perovskite membranes. However, they degrade during the oxygen permeation due to an order-disorder phase transition in the oxygen sub-lattice in which a brownmillerite phase forms [21]. The doped lanthanum cobaltite membranes, such as $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, attracted particular attention in scientific publications due to their good ionic and electronic conductivity and high chemical stability at elevated temperature [22-25]. Furthermore, the most successful modification of SCF has been $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF). For example, an oxygen permeation flux of $9.5 \times 10^{-3} \text{ mol.m}^{-2}.\text{s}^{-1}$ was acquired at 850 °C for a 1.8-mm thick disk shape BSCF membrane under the air/argon gradient [26].

$\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ materials have been extensively investigated as oxygen permeable membranes [27, 28] which possess excellent electronic and oxygen ionic conductivity at elevated temperatures. $\text{La}_{1-x}\text{Sr}_x\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ perovskites have a lower oxygen permeation flux than BSCF, however they are more mechanically stable [29, 30]. For the purpose of this study, we have considered the specific composition of $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ as it is expected to have enhanced oxygen permeation flux and high structural stability due to its high cobalt content and presence of the element lanthanum, respectively [31], [32]. The structural and chemical characteristics of perovskite membranes, and hence their subsequent performance, largely relies on the choice of temperature and dwelling time during the sintering step of the preparation process [15], with the sintering temperature having the greatest impact on the microstructure and densification of the membranes [16]. Therefore, determining the optimum sintering temperature is considered an important step in achieving the desired properties for membranes.

The specific aim of this study is to gain a better understanding of the LSCF5582 membrane oxygen separation performance under a so called reducing environment, which mimics the conditions of the CLAS process. The “reducing environment” phrase used in this manuscript refers to the environment in which oxygen carriers (e.g., CuO) are reduced to their lower oxidation state (i.e., Cu_2O) in the presence of a reducing gas (N_2). Since the performance of LSCF5582 membranes strongly relies on its structural properties and chemical composition, the study firstly determines the sintering temperature range for fabrication of the membrane for

which a dense pure single phase perovskite membrane can be obtained. This work was performed using FE-SEM and XRD as well as EDS and TGA techniques.

Moreover, the membrane performance is a function of the operating conditions, in particular its operating temperature. Hence this study examines the membrane oxygen separation properties as a function of operating temperature to obtain the optimum operating temperature for achieving maximum oxygen permeation flux and oxygen recovery. The investigation was carried out using high purity instrument air (21% O₂ and 79% N₂) on the feed side of the membranes.

Finally, the performance of LSCF5582 membranes were examined in the reducing environment of the CLAS process, in which oxygen carriers (instead of air) are used to provide oxygen on the feed side of the membrane. This in turn simulates the reduction reactor of the CLAS process where the decomposition reaction of oxygen carriers occurs. The findings from the above studies were then used to determine the optimum sintering temperature for LSCF 5582 membranes applicable to the CLAS process.

2. Experimental Materials and Procedures

Membrane preparation and characterisation

A 16 mm die set with two stainless steel anvils was used (at 130 MPa for 5 minutes) to form LSCF5582 powders with +99.99% purity and average particle size of 0.5 μm (supplied by American Elements) into disks of 1 mm thickness. The LSCF5582 green disks were then sintered at temperatures between 1050 and 1350 °C for 5 h. The sintering of materials was performed in air with heating and cooling rates of 5 °C.min⁻¹. The experimental results of the sintering process showed that the thickness of membranes remained almost unchanged (i.e. less than 2% shrinkage in the thickness) as the sintering temperature was increased from 1050 °C to 1300 °C.

For characterisation purposes, the surface morphology of membranes was observed using the Zeiss Sigma field emission scanning electron microscope (FE-SEM) equipped with Secondary electron (SE) detectors operating at 10 kV. The energy-dispersive X-ray spectrometry (EDS)

technique was also employed for the elemental analysis of the samples. The crystalline phases and structures of the membranes were identified using a Bruker D8 Advance X-ray diffractometer. The data was collected in the 2θ range of 20° - 120° with a step size of 0.013° at 25°C . The International Centre for Diffraction Data (ICDD PDF-4+ 2015) and Crystallographic Open Database (COD 2016 PANalytical version) were used to match phases.

The oxygen vacancy content (δ) of each membrane was measured as a function of operating temperature at the oxygen partial pressure of 0.21 bar. It was assumed that sample was fully oxidised initially at $t=0$, $\delta=0$. Based on literature [20], it is reasonable to consider that samples hold $\delta = 0$ value in air at room temperature provided that they are slowly treated to absorb as much oxygen as possible. The sample was then heated, at a ramp rate of $5^\circ\text{C}/\text{min}$, to 900°C under $100\text{ ml}\cdot\text{min}^{-1}$ of air flow. Then the sample was cooled down to room temperature at a cooling rate of $5^\circ\text{C}/\text{min}$ under continuous air flow. The oxygen vacancy content, δ , of each sintered membrane was calculated for the heating period ($T=25$ to 900°C) [33], as follows:

$$\delta = \left(\frac{W_0 - W(t)}{W_0} \right) \left(\frac{M_0}{M} \right) \quad (1)$$

where W_0 and M_0 are weight and the molar weight of the sample at the stoichiometric oxygen composition ($\delta = 0$) and $W(t)$ and M are sample weight at equilibrium temperature and the molar weight of oxygen atoms, respectively.

Oxygen permeation measurements

The oxygen permeation experiments were carried out using a multi tube rig with concentric $1/2''$ and $1/4''$ quartz tubes placed inside a $1''$ quartz tube (Figure 2). A membrane was sealed on the outer surface of the $1/2''$ tube using a silver paste. Three layers of silver paste were coated around the membranes during the sealing process and cured at temperatures of 180°C , 250°C and 350°C to ensure the nitrogen leak was minuscule. Perfect 100% sealing was almost unachievable in the experimental work, however, less than 3.5 % nitrogen leaked to the permeate side in accordance with the Knudsen diffusion mechanism. The leakage of nitrogen was subtracted when the oxygen permeation flux was calculated. Assuming nitrogen and oxygen leak through pores or cracks in accordance with the Knudsen diffusion mechanism [17, 29, 34], fluxes of leaked nitrogen and oxygen were related using Equation (2) as follows:

$$J_{N_2}^{leak} : J_{O_2}^{leak} = \sqrt{\frac{Mw_{O_2}}{Mw_{N_2}}} \times \frac{C_{N_2}}{C_{O_2}} \quad (2)$$

$$J_{N_2}^{leak} : J_{O_2}^{leak} = \sqrt{\frac{32}{28}} \times \frac{0.77}{0.23} = 3.5$$

where Mw_{O_2} , Mw_{N_2} , C_{O_2} and C_{N_2} are molecular weights of oxygen, nitrogen, and concentrations of oxygen and nitrogen in the permeate stream, respectively.

A thermocouple was inserted near the membrane from the top for temperature measurements. The multi tube rig was then placed inside a tube furnace (LABEC, Australia). The design details of the experimental setup can be found in the literature [35]. In order to provide the oxygen partial pressure gradient across the membrane, helium was used to constantly sweep the permeate side. Due to the robustness of using sweep gas rather than the vacuum pump, a sweep gas was selected in the experimental work presented here.

The oxygen permeation experiments were conducted for two cases. In the first case, oxygen was provided on the feed side of the membrane using air in order to examine the oxygen separation properties of membranes and also determine the optimum operating temperature for an oxygen separation application. In the second case, oxygen on the feed side of the membrane was produced through the decomposition reaction of CuO oxygen carriers with nitrogen. The second case aims to simulate the conditions in which membranes are embedded in the reduction reactor of the nitrogen based CLAS process. The experimental procedure for the two cases are explained as follow:

Permeation measurements using Air on the feed side of the membrane

A membrane was initially sealed on the outer surface of the 1/2" tube at 950 °C for an hour using the silver paste and then cooled down to room temperature. The concentric 1/2" and 1/4" tubes were then placed inside the 1" tube. Air at the flow rate of 100 ml.min⁻¹ was directed into the inlet of the 1" tube while the outlet stream was passed to the exhaust (See Figure 2). Helium at a flow rate of 50 ml.min⁻¹ swept the 1/2" tube and the outlet stream from the 1/4" tube was directed to the micro-gas chromatograph (Varian CP4900) for its compositional analysis (Figure 2). The oxygen concentration of the permeate stream was analysed every 4 minutes for

1 h at each operating temperature. A LabVIEW program was developed which recorded the temperature, pressure and mass flow rate data every 5 seconds.

The oxygen permeation flux of the membranes were calculated using Equation (3) [36-38] and any ingress of molecular air was deducted from the oxygen flux.

$$J_{O_2} = \left(x_{O_2} - \frac{21}{79} x_{N_2} \right) \frac{F}{A} \quad (3)$$

where J_{O_2} is the oxygen permeation flux ($\text{ml.cm}^{-2}.\text{min}^{-1}$), F is the permeate flow rate (ml.min^{-1}), A is the effective membrane area (cm^2), x_{O_2} and x_{N_2} are the oxygen and nitrogen mole fractions, respectively.

Permeation measurements using Oxygen Carriers on the feed side of the membrane

2 g of the CuO oxygen carrier particles were loaded into the annular space of the 1" tube and accumulated on the quartz wool. Quartz wool was used to hold particles securely in the vicinity of the membrane (See Figure 2). The membrane and tube were gently purged with dry nitrogen before assembling the top fittings to ensure particles did not cover the membrane surface. After assembling the top fittings and setting up the reactor, purging was conducted at 500 °C for 120 minutes to deplete any oxygen. The temperature of the furnace was then increased to 900 °C and held for 120 minutes. The decomposition reaction of the oxygen carrier particles in the presence of LSCF membrane was investigated at the temperature of 900 °C using 50 ml.min^{-1} of nitrogen. Helium at the flow rate of 50 ml.min^{-1} was passed through the 1/4" tube and the oxygen concentration of the permeate stream was analysed using the Micro GC every 4 minutes.

The oxygen recovery % of membranes were calculated using Equation (4) as follows:

$$\text{Oxygen Recovery (\%)} = \frac{C_{O_2, \text{permeate}} \cdot F_{\text{Sweep}}}{C_{O_2, \text{feed}} \cdot F_{\text{feed}}} \quad (4)$$

where $C_{O_2, \text{permeate}}$ is the oxygen concentration of the permeate stream, $C_{O_2, \text{feed}}$ is the oxygen concentration of the feed stream. F_{Sweep} and F_{feed} are the flow rates of sweep gas and feed streams, respectively. It should be noted that the oxygen concentration in the feed stream under

the reducing condition of the CLAS is the one liberated during the decomposition reaction of CuO oxygen carriers at equilibrium conditions.

The equilibrium concentrations of oxygen produced at 800-950 °C during the decomposition reaction of 2 g of CuO oxygen carriers (Equation 6) were obtained using a packed bed reactor (Figure 3). Initially, purging was conducted at 500 °C for 100 minutes prior to experiments to ensure that the oxygen trace in the reactor was minuscule. Figure 4 shows the oxygen depletion from the packed bed reactor in the course of purging. Afterwards, CuO oxygen carriers were reduced at 800-950 °C using nitrogen and the concentration of oxygen produced during CuO decomposition was measured using the micro-GC connected to the outlet stream from the packed bed reactor. The mass-based equilibrium conversion of CuO to Cu₂O is defined as follows [39]:

$$Conversion = \frac{m}{m_{red}} \quad (5)$$

where m and m_{red} stand for the actual mass of CuO and the equilibrium mass of CuO in a fully reduced state, respectively. In order to calculate the CuO conversion, the oxygen carrier was assumed to be in a fully oxidized state prior to each reduction cycle. Equation (6) shows the relation between moles of CuO consumed and moles of oxygen produced.

3. Results and Discussion

3.1 LSCF5582 membrane structural characteristics

FE-SEM images of LSCF5582 disk membranes for a sintering temperature range of 1050 - 1300 °C are presented in Figures 5 (a) to (f). As shown in Figures 5 (a) and (b), the membrane surface appears to be granular with a porous texture at sintering temperatures of 1050 °C and 1100 °C. That is considered to be due to the partial fusion of primary particles. At the sintering temperature of 1200 °C (Figure 5 (c)), the membrane surface was found to be smooth with distinct grain boundaries and some close end pores. Smoothness of the surface was the result of significant particle fusion taking place at elevated temperatures. At 1225 °C, the membrane density increased, however, no pores were observed at the surface of the membrane. Further

temperature increase (i.e., at 1250 °C and 1300 °C), however, led to the formation of impurities on the smooth surface of the membranes (Figures 5 (e) and (f)). Moreover, sintering at the maximum temperature of 1350 °C led to the fusion of membranes into the crucible.

EDS analysis of the impurities for La, Sr, Co, Fe and O indicated that the elemental composition of impurities were Co and O with no La, Sr or Fe elements present. The formation of cobalt oxide on LSCF5582 membranes was found to be consistent with those reported in literature for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ membranes at the sintering temperature of 1250 °C [40]. A typical result of the elemental analysis is presented in Figure 6.

The structural assessment of LSCF5582 fresh powder and membranes sintered at temperatures of 1200 °C - 1300 °C were performed using XRD (Figure 7). As Figure 7 (a) shows, LSCF membranes sintered at temperatures of 1200 -1300 °C exhibited strong peaks at $2\theta = 32.92, 40.62, 47.34, 53.83, 58.83, 69.05, 78.72, 83.32, 87.85$ and 96.99 which were attributed to Lanthanum Strontium Cobalt Iron Oxide phase (Reference code 01-089-5721) [41]. A rhombohedral crystal structure was maintained for the LSCF5582 fresh powder and membranes examined in this study. This structure was associated with $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ perovskite membranes with $y < 0.5$ [42].

At the sintering temperature range of 1250-1300 °C, in addition to the primary phase of LSCF, new weak peaks representing the secondary phase and matching cobalt (II) oxide (Reference code 01-075-0533) were observed at $2\theta = 36.60, 42.43, 61.60, 73.90$ and 78.55 . These results further confirm the earlier reports on detecting traces of CoO phase during high temperature sintering of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ with high cobalt contents and $y \leq 0.2$ [43]. An enlarged view of CoO peaks at $2\theta = 36.60$ and 42.43 is shown as an example in Figure 7 (b). As it can be seen, broad peaks at $2\theta = 40.62$ for the fresh LSCF powder reflect very fine particles, however, sharp peaks for the sintered membranes show the well-developed crystallites with larger particles. The intensity of the peaks for the cobalt oxide is far less than the actual peaks for the main perovskite phase (Figure 7 (a)).

Surfaces of the LSCF5582 membranes sintered at 1250 °C and 1300 °C were ground using sandpaper (P1200) and were examined using the backscattered electrons (BSE) and Energy Dispersive X-ray Spectroscopy (EDS) techniques. The BSE technique used an enhanced contrast image analysis approach based on the level of grey scale intensity, where the lighter

regions represent higher average atomic numbers than those of the darker regions. Figure 8 shows EDS spectrum and quantitative analyses for three spots marked on the polished LSCF membrane sintered at 1300 °C. Results showed that a CoO secondary phase segregated and formed within the grain boundaries for three spots marked in Figure 8. It should be noted that CoO was uniformly distributed along the grain boundaries of both membranes examined. Quantitative elemental analyses results acquired for three spots were very consistent and confirmed the dominant compositions of oxygen and cobalt. Therefore, it can be inferred that the secondary phase of cobalt oxide (CoO) formed internally within the membrane crystal structure and was not simply surface contamination. Similar results were obtained for LSCF membranes sintered at 1250 °C.

According to the above-mentioned results, the optimum range of sintering temperature for LSCF5582 membranes is found to be at 1200-1225 °C in which dense, single phase LSCF membranes are formed making this sintering temperature range structurally and chemically most suited for integration of LSCF5582 into the CLAS process.

3.2 LSCF5582 Oxygen separation properties using Air on the feed side of membranes

The oxygen separation properties of LSCF5582 membranes from air at a flow rate of 100 ml.min⁻¹, namely oxygen vacancy contents, permeation flux and oxygen recovery%; are presented in this section. Figure 9 shows the oxygen vacancy contents of LSCF5582 membranes calculated using Equation (1) versus the operating temperature for different sintering temperatures. As shown in this figure, oxygen vacancies at lower operating temperatures were relatively low (300 °C - 600 °C) and remained nearly constant, followed by a sharp rise, as the temperature was increased (beyond 600 °C). Desorption of alpha-type oxygen species, a weakly chemisorbed superficial oxygen species, is considered to be responsible for the observed low oxygen vacancy levels at lower operating temperatures. Whilst the desorption of bulk oxygen from the interior crystal lattice is considered to drive the increased oxygen vacancy levels at higher operating temperatures [37, 44]. The highest concentration of oxygen vacancies at the operating temperature range of 400 °C - 800 °C were

formed for LSCF membranes sintered at 1225 °C. The LSCF membranes sintered at 1300 °C had the lowest oxygen vacancy content at all operating temperatures above 550 °C. The highest membrane oxygen vacancy content was achieved when LSCF membrane, sintered at 1200 °C, was operated within the temperature range of 800 °C – 900 °C. It is expected that membranes can retain their maximum oxygen vacancies for the same operating temperature range to the CLAS process.

Figure 10 shows the oxygen permeation fluxes of LSCF5582 membranes sintered at 1200 °C - 1300 °C as a function of operating temperature. For a given sintering temperature, the oxygen permeation fluxes of LSCF5582 membranes increase with the operating temperature where the maximum oxygen permeation flux of 0.67 ml.min⁻¹.cm⁻² (27% oxygen recovery) is obtained at 900 °C. It is believed that the enhanced oxygen vacancy contents of the LSCF5582 membranes at increased operating temperature facilitates the migration of oxygen ions through the membranes and therefore improves their oxygen permeability.

At a given operating temperature, the oxygen permeation flux of the membranes decrease as the sintering temperature is increased. Sintering of membranes at increased temperatures has a negative impact on the oxygen permeability of membranes due to the formation of impurities on the membrane surface and also the grain (crystallites) growth which occurs at increased membrane sintering temperatures. Impurities (e.g., cobalt oxide) formed at increased sintering temperatures on the membrane surface add an extra resistance to the oxygen diffusion hence lower the oxygen permeation flux across the membrane. Furthermore, larger grains formed at higher sintering temperatures [45] create a greater resistance against the diffusion of oxygen ions. The oxygen permeation mechanism for 1-mm thick disk membranes examined in this work was considered to be diffusion limited consistent with literature [18, 29, 46]. In other words, grain boundaries were considered to be the fastest diffusion path for oxygen transport, hence the oxygen permeation flux decreased with increasing the membrane grain size [45, 47].

The maximum and minimum values for the oxygen permeation fluxes are obtained at the sintering temperatures of 1200 °C and 1300 °C, respectively. At any constant sintering temperature, considerably higher oxygen permeation flux is acquired at increased operating

temperatures (800-900 °C) which is desirable for enhanced separation of oxygen in the membrane integrated nitrogen based CLAS process.

3.3. LSCF5582 Oxygen recovery% and permeation flux under the reducing environment of N₂ in the presence of CuO oxygen carriers

The equilibrium concentrations of oxygen liberated during the decomposition reaction of CuO oxygen carriers under the reducing environment were measured over the operating temperature range of 800 – 950 °

C, Figure 11, using the packed bed reactor. As Figure 11 (a) shows, at 800 °C, there was no significant change in the oxygen concentration of the outlet stream from the packed bed reactor over a period of 100 minutes since the decomposition reaction of CuO is relatively slow. At 900 °C, the oxygen concentration and CuO conversions sharply increased during the first 50 minutes of the experiment after which they reached their equilibrium value of 0.159 % (Figure 11(b)). A stable 100% equilibrium CuO conversion at 900 °C conveys that that the equilibrium concentration of oxygen produced levels off at 0.159 % after 50 minutes and the reduction reaction (Equation 6) does not proceed any further with time at this equilibrium temperature. The highest concentration of oxygen (0.38%) in the outlet stream from the packed bed reactor was recorded at 950 °C (Figure 11(c)). This concentration was reached only after 24 minutes, however the concentration rapidly dropped indicating that CuO was fully consumed and converted to Cu₂O before completion of the experiment. The rise in the conversion of CuO and the concentration of oxygen liberated during the decomposition reaction with increased temperature is supported by Le Chatelier's principle.

Figure 12 shows oxygen concentration % in the permeate stream of LSCF5582 membranes with sintering temperatures ranging between 1200 °C and 1300 °C under the reducing environment as a function of time. These results were obtained at the operating temperature of 900 °C. The optimum operating temperature of 900 °C was selected for the measurements as the performance of membranes and oxygen carriers were well matched at this particular temperature. This temperature was selected according to the results of the oxygen permeation

of the membranes presented in the previous sub-section (i.e., 3.2) and the current ones mentioned above for the decomposition reaction of the oxygen carriers.

In Figure 12, it was expected that the oxygen concentration recovered with LSCF sintered at 1200 °C to be the greatest (based on the general trend presented in Figure 10), however data obtained for LSCF at 1200 °C did not follow this trend. The observed trend might be due to the residual of oxygen carriers left on the surface of the membrane which reacted with the LSCF membrane at the operating temperature of 900 °C and hence added extra resistance against the oxygen diffusion resulting in lower oxygen flux. The highest oxygen concentration of 0.13% was recovered with the LSCF5582 membranes sintered at 1250 °C, however, the membranes cracked as 100 minutes elapsed (See Figure 13). A similar failure has been reported in literature for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ disc membrane during oxygen permeation experiments at 950 °C [48]. Mechanical stress due to a mismatch between the thermal expansion coefficients of the membrane and the sealant is considered as the main reason behind the observed cracking. Amongst multiple experiments conducted, it was observed that cracking was more prevalent for membranes sintered at 1250 °C and 1300 °C. The lowest oxygen concentration (0.041%) was obtained with the LSCF5582 membrane sintered at 1300 °C. The formation of impurities on the membrane during sintering at high temperatures is believed to be responsible for the membranes low separation efficiency. Between sintering temperatures of 1200 °C and 1250 °C, an increase in sintering temperature led to an increase in the concentration of oxygen in the permeate stream rising from a value of 0.079% to 0.13%.

Oxygen permeation fluxes and oxygen recovery% of LSCF membranes at the operating temperature of 900 °C as a function of sintering temperatures are presented in Table 1. It can be seen that higher oxygen flux and recovery were obtained with LSCF5582 membranes at sintering temperatures of 1200 °C and 1250 °C. However, the lowest oxygen recovery was acquired for the LSCF5582 membrane sintered at 1300 °C which is believed to be due to its low oxygen permeation properties.

It was found that even though the LSCF5582 membrane sintered at 1250 °C showed the highest oxygen flux during the CuO decomposition period, its mechanical instability during the permeation experiments makes it unfavourable for its utilisation in the nitrogen based CLAS

process. The LSCF5582 membrane sintered at 1225 °C, on the other hand with demonstrated high oxygen permeation flux of $0.77 \text{ ml.min}^{-1}.\text{cm}^{-2}$, as well as its structural stability during the decomposition reaction, was found to have the most suitable properties for integration into the nitrogen based CLAS process.

4. Conclusions

In this study, $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membranes prepared at different sintering temperatures were characterised from chemical and structural perspectives to determine the optimum sintering temperature range for integration into the nitrogen based CLAS process for enhanced oxygen separation. FE-SEM images showed that the LSCF5582 membranes densified at the sintering temperature range of 1200 -1225 °C. EDS elemental analysis together with XRD results showed that a secondary phase of cobalt oxide appeared on the surface of LSCF5582 membranes sintered at temperatures greater than or equal to 1250 °C. The XRD results indicated a rhombohedral crystal structure for all LSCF5582 membranes examined in this work. The oxygen permeation experiments using 100 ml.min^{-1} air at 900 °C showed a maximum oxygen recovery of 27% and an oxygen permeation flux of $0.67 \text{ ml.min}^{-1}.\text{cm}^{-2}$ for LSCF5582 membranes sintered at 1200 °C. Based on the structural and chemical characteristics of LSCF5582 membranes, the optimum range of sintering temperature was considered to be 1200-1225 °C.

Furthermore, the highest oxygen recovery of 76% and oxygen flux of $0.77 \text{ ml.min}^{-1}.\text{cm}^{-2}$ in the presence of CuO oxygen carriers were obtained using the LSCF5582 membranes sintered at 1225 °C. The optimum operating temperature for the membranes and CuO oxygen carriers were 900 °C, as the performance of the membranes and oxygen carriers were well matched. According to the above investigation the LSCF5582 membrane sintered at 1225 °C is considered to be the most suited LSCF5582 membrane for integration into nitrogen based

CLAS, due to its high structural stability during the decomposition reaction as well as its high oxygen recovery performance.

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Figure 1: A schematic of membrane integrated Nitrogen based CLAS process.

Figure 2: Schematic diagram of the multi tube rig and the inset photo of CuO packed in the vicinity of a membrane.

Figure 3: A schematic of the packed bed reactor used to determine the equilibrium concentrations of oxygen produced during CuO decomposition at 800-950 °C with 50 ml.min⁻¹ nitrogen.

Figure 4: The variations in oxygen concentrations with time during purging the packed bed reactor with $50 \text{ ml} \cdot \text{min}^{-1}$ nitrogen at 500°C .

(a)

(b)

(c)

(d)

(e)

(f)

Figure 5: FE-SEM images of LSCF5582 disk membranes sintered at (a) 1050 °C, (b) 1100 °C, (c) 1200 °C, (d) 1225 °C (e) 1250 °C and (f) 1300 °C.

Figure 6: Elemental map of (a) LSCF5582 membranes sintered at 1250 °C for traces of (b) La, (c) Sr, (d) Co, (e) Fe and (f) O. Colours blue, red, green, light blue and purple correspond to La, Sr, Co, Fe and O, respectively, while black indicates the absence of the element.

(a)

(b)

Figure 7: XRD analysis of LSCF5582 fresh powder and membranes (a) sintered at the temperature range of 1200 °C to 1300 °C (b) extra peaks representing CoO compound formed at 1250 °C and 1300 °C at $2\theta = 36.60$ and 42.43 .

(a)

(b)

(c)

Element	(wt.%)	(at.%)
Oxygen	17.46	43.83
Magnesium	0.35	0.59
Cobalt	81.14	55.28
Lanthanum	1.05	0.30

(d)

Element	(wt.%)	(at.%)
Oxygen	19.06	46.43
Magnesium	0.46	0.73
Cobalt	79.49	52.56
Lanthanum	0.99	0.28

(e)

Figure 8: (a) BSE image of the polished LSCF5582 membrane sintered at 1300 °C, EDS spectrum for spots (b) 1 and (c) 3 and weight percentage as well as atomic percentage quantitative elemental analyses for spots (d) 1 and (e) 3.

Figure 9: Oxygen vacancy contents of LSCF5582 membranes versus operating temperature for different sintering temperatures (0.21 bar oxygen partial pressure, 100 ml.min⁻¹ of air).

Figure 10: Oxygen permeation fluxes of LSCF5582 membranes sintered at 1200 °C - 1300 °C as a function of operating temperature measured at 100 ml.min⁻¹ air and 50 ml.min⁻¹ helium flow rates using the multi tube setup.

(a)

(b)

(c)

Figure 11: The variations in oxygen concentrations and CuO conversions with time during the decomposition reaction of CuO at (a) 800 °C (b) 900 °C and (c) 950 °C using 50 ml.min⁻¹ nitrogen as a reducing gas. The results are per 2 g of oxygen carrier containing 17 wt% active CuO.

Figure 12: The concentrations of oxygen liberated at the operating temperature of 900 °C recovered with LSCF5582 membranes sintered at temperatures of 1200 °C - 1300 °C during the decomposition period of 2g of CuO using 50 ml.min⁻¹ nitrogen.

Figure 13: Cracks observed on LSCF5582 membrane sintered at 1250 °C after 100 minutes elapsed from the permeation experiment.

Table 1: The calculated oxygen fluxes and oxygen recoveries of LSCF5582 membranes during the decomposition of CuO at the operating temperature of 900 °C at different sintering temperatures.

Sintering temperature (°C)	Oxygen concentration (%)	Oxygen permeation flux (ml.min⁻¹.cm⁻²)	Oxygen recovery (%)
1200	0.08	0.34	50
1225	0.12	0.77	76
1250	0.13	0.92	83
1300	0.04	0.09	26