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Effect of microstructure and thickness on oxygen permeation of $La_2NiO_{4+\delta}$ membranes

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Abstract

Lanthanum nickelate, La_2NiO_4 (LNO) powders were synthesized by a sol–gel method. These powders were compacted to obtain LNO membranes. The grain size effect on the permeation of LNO membranes was examined by variation of the sintering time of membranes from 5 to 48 h. The microstructure of membranes was analyzed using scanning electron microscopy (SEM) and the grain size was determined using a statistical approach. The grain size was observed to increase with the dwell time following a power law. The permeation of the membranes increased with increasing dwell time up to 15 h. For dwell time of 48 h, the permeability decreased sharply. The oxygen permeation of LNO membranes was also measured as a function of membrane thickness in the same temperature range. With the aim of looking at the effects of bulk diffusion and kinetics of surface-exchange, the membrane thickness was varied from 0.8 to 1.3 mm. The characteristic critical thickness (L_C) of the membrane, at which the surface exchange kinetics becomes dominant, was found to be 1.0 mm in the temperature range of 700–1000 °C.

Keywords: A. Sintering; A. Sol-gel processes; B. Grain size; D. Perovskites; Oxygen transport membranes

1. Introduction

Ceramic ion transport membranes (ITM) that exhibit high oxygen ionic and electronic conductivity have been a great choice for producing oxygen by separation from air. The oxygen production by these ion transport membranes is quite economical, clean and efficient. La_2NiO_4 (LNO) is one of the potential materials for oxygen permeability as it shows a good permeation flux and also exhibits higher stability as compared to the other materials [1]. The crystal lattice of LNO is similar to the K_2NiF_4-type and can be described as a succession of perovskite layers alternating with rock salt LaO layers [2]. The thermodynamic stabilities for the K_2NiF_4-type materials is known to be higher than the perovskite-type oxides [3]. Skinner and Kilner [4] found that the oxygen transport properties of La_2NiO_4 were almost equivalent to $La_{0.3}Sr_{0.7}CoO$ (LSC) and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) along with the advantage of being thermo-mechanically stable at elevated temperatures. X-ray diffraction spectra at elevated temperatures show that LNO is stable in air up to more than 1300 °C [5]. LNO also shows excellent long term stability with even 100% CO_2 in the sweep [6]. Yaremchenko et al. [7] studied the permeability and the stability of $La_2Ni_{0.9}Co_{0.1}O_{4+\delta}$ membranes under a reducing environment of hydrogen and observed that membranes were quite stable at 973 K. Bassat et al. [8] compared the ionic conductivities of K_2NiF_4-type structures (LNO, PNO) and the perovskite structures (LSCF, LSFN) and observed that the K_2NiF_4-type structures gave better results especially at lower temperatures. The rate of permeation of oxygen through these oxygen selective ITMs depends on two factors: one is the solid state diffusion rate through the membrane and the second factor is the rate of exchange of oxygen ions on the feed and permeate sides of the

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membrane [9]. The oxygen permeability also increases with increasing temperature and partial pressure of oxygen [10].

To obtain further improved membranes one of the areas in the focus is to optimize microstructure and processing parameters. Arnold et al. [11] prepared perovskite-type membranes $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) and $Ba_{0.5}Sr_{0.5}Fe_{0.8}Zn_{0.2}O_{3-\delta}$ (BSFZ) using boron nitride (BN) as sintering aid. They studied the average grain size of these membranes as a function of the amount of BN used. They concluded that a smaller grain size lowers the oxygen permeability (especially for BSCF). In addition, Shaula et al. [12] in their study on $CaTi_{0.8}Fe_{0.2}O_{3-\delta}$ membranes suggesting that grain boundaries act as barriers for oxygen permeation. Furthermore, Klande et al. [13] prepared BSCF and SCF membranes of varying grain sizes by using different dwell times during the sintering step of membrane preparation. They have determined that the flux in BSCF membranes was independent of the grain size in the range of 24–42 µm, but smaller grains showed a decreased oxygen flux. In contrast, Diethelm et al. [14] showed that the membranes prepared from $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ with larger grains (i.e fewer grain boundaries) had smaller oxygen permeation than the ones with smaller grains. In addition, Klande et al. [13] showed that the oxygen flux has decreased with larger grains for $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) membranes. Similarly, Zeng et al. [15] studied the effects of sintering temperature on phase structure, microstructure, oxygen nonstoichiometry, electrical conductivity and oxygen permeation of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membranes. They suggested that although the phase structure and oxygen nonstoichiometry of the membranes largely remained unchanged, there was significant effect on the microstructure and the electrical conductivity, which in turn would have an effect on the oxygen permeability. They showed that the grain boundaries have a much lower electrical conductivity than the bulk.

Membrane thickness is another issue to consider for oxygen permeability. In order to increase the oxygen flux, the thickness of the membrane is often reduced. When this thickness becomes lower than a certain value, the surface kinetic reactions start to limit oxygen permeation more than the bulk diffusion [16]. This thickness value is often known as the critical thickness (L_c). It is a temperature dependent quantity and has been reported to vary from 20 to 3000 µm in mixed conducting materials depending on the composition and oxygen partial pressure [17–21]. Haworth et al. [22] determined the critical thickness of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.175}Y_{0.025}O_{3-\delta}$ (BSCFY) hollow fiber membrane to be around 0.4 mm. They also deposited silver catalyst to further enhance the permeation flux below the critical thickness in the temperature range of 650–900 °C. Wiik et al. [23] studied the critical thickness of $SrFe_{1-x}Co_xO_{3-\delta}$ as a function of cobalt content and found out that L_c decreased from 2 mm to 0.7 mm when 67% cobalt was added. Zhu et al. [24] prepared cobalt free perovskite $BaCe_{0.15}Fe_{0.85}O_{3-\delta}$ and found its critical thickness to be 0.78 mm in the temperature range of 750–950 °C. Hong and Choi [16] determined the critical thickness of BSCF to be 1.1 mm at 900 °C.

According to our literature search, there is a lack of any study on the effect of grains size on the performance of the LNO membranes. In this work, the effects of varying microstructure and thickness on the oxygen permeability of LNO membranes are discussed. In addition, the critical thickness of LNO membranes is determined in the temperature range of 700–1100 °C.

2. Experimental procedure

2.1. Membrane processing and characterization

The La_2NiO_4 (LNO) powders were prepared using a sol gel method. The nitrates of lanthanum and nickel were mixed in stoichiometric proportions using citric acid and ethylene glycol as the chelating and polymerization agents respectively. The solution was stirred and heated to obtain a green viscous gel, which was then calcined at about 1000 °C to obtain the LNO powder. The powder was compacted at a force of 10,000 lb and sintered at a temperature of 1500 °C. Typically, sintering time of 10 h was used but in order to study the effect of sintering time on the microstructure and the performance of the LNO membranes, other sintering durations of 5, 15 and 48 h were performed. The heating and cooling rates during sintering were kept to be 2 °C/min in order to avoid any cracks on the membrane. Before testing the permeability, the membranes were polished to achieve the required thickness. Membranes with final thickness of 1.3 mm, 1.2 mm, 1.1 mm, 1.0 mm and 0.8 mm were prepared. The density of the sintered membranes was measured using Archimedes' method. The X-ray diffraction data was recorded at room temperature to observe the final crystal structure of the membranes. Angular range (2θ) was from 20° to 60° with a step size of 0.02 °/min. The microstructure of the membrane was studied using scanning electron microscopy (SEM). Energy Dispersive X-ray Spectroscopy (EDS) was used to confirm the composition of the membranes.

2.2. Oxygen Permeability Measurement

The schematic experimental setup for the measurement of oxygen permeation flux is shown in Fig. 1. The actual setup has been published elsewhere [25]. This apparatus consisted of two aligned sets of alumina tubes separated with the LNO membrane inside a split furnace. Each alumina set was considered as a chamber composed of two coaxial ceramic tubes. In each ceramic chamber, the gas flew from the inner tube towards the membrane and exited through the outer tube. A thermocouple was placed in the upstream chamber and used to measure the actual temperature at the membrane's surface. The membrane was heated in the split furnace to the final temperature at a heating rate of 2 °C/min. During heating, a paste made from mixture of ceramic powder and borosilicate glass was used to seal the membrane with the outer alumina tubes. Permeability data was collected in the temperature range of 700–1100 °C. Natural air was introduced at a flow rate of 20 ml/min in the upstream chamber using a mass flow controller. On the permeate side, downstream chamber, Helium was used as a sweep gas at a flow rate of 30 ml/min. The output gas of the downstream chamber was analyzed using a gas chromatograph.