Chemical Engineering Science 101 (2013) 240–247

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

CO_2-tolerant alkaline-earth metal-free single phase membrane for oxygen separation

Qin Zheng, Jian Xue, Qing Liao, Yanying Wei, Zhong Li, Haihui Wang*

School of Chemistry & Chemical Engineering, South China University of Technology, No. 381 Wushan Road, Guangzhou 510640, China

HIGHLIGHTS

- A CO_2-tolerant alkaline-earth metal-free single phase membrane made of $(Nd_{0.9}La_{0.1})_2Ni_{0.74}Cu_{0.21}Ga_{0.05}O_{4+\delta}$ is developed.
- A stable oxygen permeation flux of 0.53 ml/min cm^2 was achieved with pure CO_2 as the sweep gas during 420 h.
- The NLNCG membrane possesses a good oxygen permeation flux and an excellent stability under pure CO_2 atmosphere.

ARTICLE INFO

Article history:
Received 20 March 2013
Received in revised form
15 June 2013
Accepted 20 June 2013
Available online 27 June 2013

Keywords:
Membranes
Separations
Gases
Combustion
K_2NiF_4 structure
Selectivity

ABSTRACT

A novel CO_2-tolerant alkaline-earth metal-free single phase membrane based on $(Nd_{0.9}La_{0.1})_2Ni_{0.74}Cu_{0.21}Ga_{0.05}O_{4+\delta}$ (NLNCG) was successfully prepared though a sol–gel route. The oxygen permeation and the stability of the NLNCG under CO_2 are investigated in detail. At 975 °C, when helium is used as the sweep gas, the oxygen permeation flux of 0.53 ml/min cm^2 (STP) is obtained. When the sweep gas is changed from helium to CO_2, the oxygen permeation flux is reduced to 0.48 ml/min cm^2 (STP). Only a slight decrease of the oxygen permeation flux through the NLNCG membrane is observed. During the 420 h operation with CO_2 as the sweep gas at 975 °C, a steady oxygen permeation flux through the NLNCG membrane of 0.53 ml/(min cm^2) is obtained. From XRD and SEM characterizations, it is found that the spent membrane still maintains the perfect K_2NiF_4-type phase structure and intact microstructure without any carbonate indicating that the NLNCG membrane shows an excellent stability under CO_2 atmosphere.

1. Introduction

Recently, CO_2 capture and storage technologies have received great interest because they can reduce the emission of CO_2 which is considered as the main contribution to the global warming (Olajire, 2010; Sunarso et al., 2011 ; Figueroa et al., 2008; Gough, 2008; Kneer et al. , 2010). So far, post-combustion, pre-combustion and oxy-fuel combustion are three major concepts for CO_2 sequestration. (Figueroa et al., 2008; Gough, 2008) A process which is becoming attractive rapidly is the oxy-fuel combustion, i.e. burning coal or natural gas with pure O_2 or O_2/CO_2 mixture instead of air. This is reflected by several projects around the world including CS Callide (Australia), Vattenfal (Germany), and Inabensa (Spain) while oxy-fuel coal combustion is the process of choice for the rejuvenated FutureGen (USA) program. (Sunarso et al., 2011) Mixed oxygen ionic-electronic conducting ceramic membranes (MIECMs) have gained increasing attention due to their potential applications in the oxygen supply to power stations for the oxy-fuel combustion with CO_2 sequestration (e.g. according to the oxy-fuel concept (Kneer et al.,2010; Bredesen et al., 2004; Tan et al., 2008)). In the oxy-fuel process, oxygen diluted with recycled CO_2 is used to burn fossil fuels, resulting in a flue gas mainly consisted of CO_2 and H_2O which can be easily separated by condensation. Therefore, the membrane was exposed to CO_2 with high concentration. For this reason, the mixed conducting oxygen permeable membrane applied in oxy-fuel process not only should have good oxygen permeability, but also good stability especially under the atmosphere with high concentration of CO_2.

Most studies of the mixed conducting oxygen permeable membrane have been concentrated on the perovskite-type oxides which have relatively high oxygen permeation fluxes (Teraoka et al., 1985; Kharton et al., 1998; Nagai et al., 2007; Qiu et al., 1995; Elshof ten et al., 1995; Tsai et al., 1998; Teraoka et al., 1985; Shao et al., 2000; Li et al., 2010; Yin and Lin, 2006; Yin et al., 2006; Qi et al., 2003). Unfortunately, the perovskite materials are quite sensitive to CO_2 because they contain alkaline-earth elements such as Ba and Sr on the A-site, which can easily react with CO_2 and SO_2 to form the carbonates and sulfates (Arnold et al., 2007; Yi et al., 2010; Yang et al., 2009; Czuprat et al. 2010; Martynczuk et al., 2009; Yang et al., 2006; Tong et al., 2002; Yi et al., 2005; Park et al., 2009; Jin et al., 2006; Jin et al., 2008). Several groups (Arnold et al., 2007; Yi et al., 2010; Yang et al., 2009;

* Corresponding author. Tel./fax:+86 020 87110131.
E-mail address: hhwang@scut.edu.cn (H. Wang).

0009-2509/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ces.2013.06.039

Czuprat et al. 2010; Martynczuk et al., 2009; Yang et al., 2006; Tong et al., 2002) found that the oxygen permeation fluxes through the perovskite membranes containing alkaline-earth elements have a serious decrease due to the formation of carbonate even when a very low concentration of CO_2 was introduced into the sweep gas. For example, Arnold et al. (2007) observed an immediate stop of the oxygen permeation for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) membrane when CO_2 was used as sweep gas at 875 °C. Yang et al. (2006) demonstrated that the perovskite structure of $La_{0.1}Sr_{0.9}Co_{0.5}Fe_{0.5}O_{3-\delta}$ (LSCF) decomposed to carbonate and metallic oxide phases after a desorption process by using CO_2 as sweeping gas treatment at 800 °C.

One effective way to overcome the aforementioned problems is to avoid alkaline-earth metals in the MIEC material. Recently, several free-alkaline-earth metals dual phase membranes made of an ionic conductor and an electronic conductor, are proposed as alternatives, because these oxides possess inherently high chemical stability against these acidic or reducing gases. For example, Luo et al. (2011a, 2011b) developed a novel alkaline-earth metal-free dual-phase CO_2-tolerated oxygen permeable membrane, which exhibits excellent stability under CO_2-containing atmosphere , but the oxygen permeation flux is relatively low. Zhu et al. (2012) designed another dual-phase membrane for CO_2 capture with higher oxygen permeation flux, while this dual-phase membrane still contains 3% alkaline earth metal which could have a negative effluence on the long-term stability in the practical application of high CO_2 concentration. Recently, Zhang et al. (2012) reported a new CO_2-tolerant ion-transporting ceramic membrane with an external short circuit for oxygen separation. This membrane system shows an appreciated oxygen permeation flux at intermediate temperatures, however, the expensive noble metal layer and noble metal sealing were used; their high prices turn out as a drawback.

Recently, Yashima et al.(2010) found that a K_2NiF_4-type MIEC material based on $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_{4+\delta}$ (PLNCG) exhibits a significant level of electronic conductivity. They demonstrated that the oxygen permeation rate of PLNCG using He as sweep gas is quite high in comparison with the conventional $ABO_{3-\delta}$ perovskite-type MIECs in the literature. However, the chemical stability and oxygen permeability under CO_2 were not studied yet. Our group found that the $(Pr_{0.9}La_{0.1})_2Ni_{0.74}Cu_{0.21}Ga_{0.05}O_{4+\delta}$ (PLNCG) exhibits an excellent stability under CO_2 (Tang et al., 2012). However, the oxygen permeation flux of the PLNCG is 0.32 ml/(min cm^2) at 975 °C using pure CO_2 as sweep gas, which is relatively low. Nd and Pr are in the same group of La series so that they possess similar properties, while Nd–O bond energy is lower than Pr–O bond energy (Lide et al., 2010), which may incorporate more excess oxygen in the structure and improve the oxygen permeability. It was also found that the doping of the elements which have lower bond energy in the K_2NiF_4 structure may introduce an excess oxygen in the structure and contribute to a higher oxygen permeation flux (Akihiro and Tatsumi, 2010). In addition, it was found that the $Nd_2NiO_{4+\delta}$ exhibits a higher range of variations in the oxygen nonstoichiometry which is good for improving the oxygen permeabilities (Ziesche et al., 2008). Therefore, we chose Nd to substitute Pr in PLNCG and developed a new material named $(Nd_{0.9}La_{0.1})_2Ni_{0.74}Cu_{0.21}Ga_{0.05}O_{4+\delta}$ (NLNCG). It is expected that the NLNCG membrane could have a high oxygen permeability and good stability under CO_2 atmosphere.

2. Experimental

2.1. Synthesis of powder and membrane

The NLNCG powder was synthesized via a combined citrate and EDTA complexing sol–gel method (Wang et al., 2005). Appropriate amount of $Nd(NO_3)_3.xH_2O$, $La(NO_3)_3.6H_2O$, $Ni(CH_3COO)_2.4H_2O$, $Cu(NO_3)_2.3H_2O$ and $Ga(NO_3)_3$ were dissolved in the distilled water followed by the addition of citric acid, ethylene diamine tetraacetic acid (EDTA), and $NH_3.H_2O$. After evaporating to dryness of a mixed aqueous solution containing appropriate amounts of metal salts, the residue was ignited to flame to get the precursor. The precursor was ground and calcined at temperature up to 950 °C for 10 h with a heating rate of 2 °C/min to remove the residual carbon and form the desired $K_2NiF_{4+\delta}$-type structure. The as-prepared oxide powder was isostatically pressed into disk membrane in a stainless steel module at 20 Mpa, and then sintered at 1250 °C in air for 10 h. The thickness of sintered disk membranes was related to the amount of fresh powder and the sintered temperature. The diameter of the membrane is around 14 mm. The relative density of the sintered membrane is around 95%.

2.2. Characterization of membrane materials

The as-prepared NLNCG powder was heated to 950 °C in a gas mixture of CO_2 and N_2 with the total flow rate of 50 ml/min and keep at 950 °C for 1 h, followed with cooling to room temperature. The phase structure of the as-prepared NLNCG powder was characterized by X-ray diffraction (XRD, Bruker-D8 ADVANCE, Cu Ka radiation) in the 2θ range of 10° to 95° with a step width of 0.02°. The microstructure and morphology of the sintered NLNCG disk membrane and the spent membrane were observed by scanning electron microscopy (SEM, HITAGHI S-3700 N).

2.3. Oxygen permeation

The oxygen permeation fluxes through the NLNCG membranes were investigated by the gas chromatography (GC) method in a home-made high-temperature oxygen permeation apparatus which was described in detail elsewhere (Wang et al., 2005). A ceramic sealant (Huitian Adhesive Enterprise, Hubei, China) was used as the sealant to seal the disk-shaped membranes onto the ceramic tube. Dried air was fed to the air side of the membrane, and He/ CO_2 was fed to the sweep side. Flow rates of gases were controlled by mass flow controllers (MFC, Seven Star D08-4 F/ZM). The effluents were detected by an on-line gas chromatograph (GC, Agilent Technologies, 7890 A). To ensure the reliability of the experimental data, the GC was frequently calibrated using the standard gases of oxygen, helium, CO_2 and the flow rates were regularly calibrated by using a bubble flow meter. Assuming that leakage of nitrogen and oxygen through pores or cracks is in accordance with Knudsen diffusion, the fluxes of leaked N_2 and O_2 are related by $J_{N_2}^{Leak} : J_{O_2}^{Leak} = \sqrt{32/28} \times 0.79 : 0.21 = 4.02$. The O_2 permeation flux was then calculated as follows (Wang et al., 2002):

$$J_{O_2}(\mathrm{ml/min\cdot cm^2}) = \left[C_{O_2} - \frac{C_{N_2}}{4.02}\right]\frac{F}{S} \quad (1)$$

where C_{O_2}, C_{N_2} are the oxygen concentration and nitrogen concentrations calculated from the GC measurements, F the flow rate of the sweep stream, which can be measured by the soap flow meter, and S the membrane area.

3. Results and discussion

Fig. 1 presents the XRD patterns of the NLNCG powder samples before and after exposure to CO_2 with different concentrations at 950 °C for 1 h. The powder keeps its original $K_2NiF_{4+\delta}$ structure and no carbonate reflections are observed when the NLNCG powder was exposed to CO_2-containing atmosphere even pure CO_2, which indicates the NLNCG membrane exhibits an excellent