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Carbon dioxide permeation properties and stability of samarium-doped-ceria carbonate dual-phase membranes

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ABSTRACT

This study examines high temperature carbon dioxide permeation properties and long-term permeation stability of samarium doped ceria (SDC)-carbonate dual-phase membranes. Hermetic SDC-carbonate membranes were prepared by infiltrating porous SDC ceramic support with Li/K/Na molten carbonate. Carbon permeation experiments on the SDC-carbonate membranes were conducted with either atmospheric or high pressure feed of CO_2:N_2 mixture or simulated syngas with composition of 50% CO, 35% CO_2, 10% H_2, and 5% N_2. The SDC-carbonate membranes exhibit CO_2 permeation flux in the range of 0.2–0.8 mL(STP) cm^{-2} min^{-1} in 700–950 °C with measured CO_2 to N_2 separation factor above 1000. The CO_2 permeation flux shows power function dependence with CO_2 partial pressure and exponential dependence with temperature. The activation energy for CO_2 permeation is 63 kJ mol^{-1}, similar to that for oxygen ionic conduction in SDC. Essentially the same CO_2 permeation characteristics are observed for the membranes with CO_2:N_2 and simulated syngas feeds. The membranes exhibit stable long-term permeation flux in 700–900 °C with either CO_2:N_2 or simulated gas feed at atmospheric pressure or high pressure (5 atm) for various periods of testing time (as long as 35 days). The membranes, with remarkable permeation stability in the presence of H_2, show only slight decomposition of the ceramic phase after long-term exposure to feed gas mixtures at high temperature.

1. Introduction

There are many potential applications for inorganic membranes perm-selective to carbon dioxide at high temperatures in separation and reaction processes involving CO_2, including carbon dioxide capture technologies at large point sources, like power plants. The three main strategies considered for carbon capture from power plants include: post-combustion, oxy-fuel combustion, and pre-combustion [1,2]. In post-combustion capture, CO_2 is separated from flue gas after fossil fuel combustion. In oxy-fuel combustion, oxygen replaces air during combustion, mainly producing H_2O and CO_2, which is then separated. In pre-combustion capture, fossil fuels are reformed to produce syngas, which is mainly composed of CO and H_2. Syngas then undergoes water-gas shift reaction to produce more hydrogen, resulting in a high pressure CO_2 and H_2 stream, which is then separated. Pre-combustion capture offers the advantages of producing a high purity, carbon-free fuel as well as high pressure capture of CO_2 [3]. Of the potential technologies for pre-combustion capture, inorganic membranes offer the advantages of being temperature resistant, being able to handle large flow rates, and having a relatively small footprint.

The development of CO_2 selective membranes for pre-combustion capture is a considerable challenge, as it requires the separation of larger CO_2 from smaller H_2. In addition, polymeric and inorganic membranes are both limited in their separation performance at high temperatures. To improve upon these limitations, the concept of a CO_2-selective dual-phase dense membrane consisting of a metallic and molten carbonate phase was proposed [4]. By taking advantage of the conducting properties of both the stainless steel support and infiltrated molten carbonate, CO_2 can be selectively separated from a gas mixture by reacting with oxygen on the membrane surface, resulting in a permeable carbonate ion. This concept, however, has shown stability concerns at high temperature. Recent work on a silver-carbonate dual-phase membrane has shown an improvement of CO_2 permeance, but with similar limitations at high temperature [5]. An additional limitation of the metal-carbonate dual-phase membrane is that the presence of oxygen is required in order to form a permeable carbonate ion, resulting in the separation of CO_2 and O_2 from a gas mixture.

To improve upon these limitations, the use of an oxygen ion conducting ceramic was proposed in place of the metallic support [6]. As shown in Fig. 1, using an ionic conducting support, a carbonate ion is formed by the reaction of CO_2 with lattice oxygen ions in the ceramic phase, rather than gaseous O_2:

$$CO_2 + O^{2-} \leftrightarrow CO_3^{2-} \tag{A}$$

The CO_2 partial pressure difference across the membrane provides the driving force for carbonate ion permeation, and on the permeate membrane surface, CO_2 is released from the carbonate phase and

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oxygen ions return to the ceramic phase. Recently, modeling work has reported CO_2 transport though ceramic-carbonate membranes using ionically conductive ceramic supports [7,8].

The first ceramic support used to report experimental CO_2 permeation in the dual-phase membrane was the oxygen ionic-electronic mixed-conducting perovskite-type material $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF) [9]. Using a eutectic Li/Na/K molten carbonate, LSCF-carbonate membranes of about 0.4–3 mm in thickness showed CO_2 separation from Ar and N_2 at temperatures ranging from 700 to 900 °C, with a maximum measured CO_2 permeance of 4.7×10^{-8} mol m^{-2} s^{-1} Pa^{-1} and CO_2/N_2 selectivity of at least 225, respectively. Since then several groups have reported on synthesis of ceramic-carbonate dual-phase membranes either of smaller membrane thickness or using ionic-conducting metal oxides as the support. Yttria-stabilized-zirconia (YSZ)-carbonate and gadolinia doped ceria-carbonate dual-phase membranes of 200–400 μm thick have shown CO_2 permeances of 2×10^{-8} and 3×10^{-8} mol m^{-2} s^{-1} Pa^{-1}, respectively at 850 °C [10]. A 10 μm YSZ-carbonate membrane has shown a CO_2 permeance of 7.69×10^{-8} mol m^{-2} s^{-1} Pa^{-1} at 650 °C [11]. $B_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (BYS)-carbonate modified with γ-alumina has also been prepared and measured a CO_2 permeance of 1.1×10^{-8} mol m^{-2} s^{-1} Pa^{-1} at 650 °C [12]. Zhang et al. [13] reported very high CO_2 permeance (1.35×10^{-7} mol m^{-2} s^{-1} Pa^{-1} in the presence of H_2 at 700 °C) for a 1.2 mm thick $Ce_{0.8}Sm_{0.2}O_{1.9}$-carbonate membrane [13]. All these studies were focused on synthesis and initial CO_2 permeation properties of ceramic-carbonate membranes at high temperatures and atmospheric pressure. Little was done to examine the long term stability or the effect of increased system pressure on the permeation performance of the ceramic-carbonate membrane. For industrial applications, especially for pre-combustion processes, long term stability and an ability to withstand large system pressures will be necessary.

Recently, stability studies were conducted on LSCF-carbonate [14] and $La_{0.85}Ce_{0.1}Ga_{0.3}Fe_{0.65}Al_{0.05}O_{3-\delta}$ (LCGFA)-carbonate [15] membranes under the conditions of CO_2 permeation and separation. LSCF-carbonate membranes have shown poor stability in the absence of O_2, as the membrane surface reacts with CO_2, resulting in a carbonate surface layer that limits the surface exchange reaction between CO_2 and lattice oxygen. LCGFA-carbonate membranes have shown high chemical stability in the presence of simulated syngas conditions, as well as stable CO_2 permeation for one month at high 900 °C. However, limited ionic conductivity of the ceramic phase results in a relatively low CO_2 permeance relative to other materials previously studied.

In an effort to improve the stability of the dual-phase membrane in harsh experimental conditions and maintain a high CO_2 permeation flux, the fluorite-type ceramic material samarium doped ceria (SDC) with composition $Ce_{0.8}Sm_{0.2}O_{1.9}$ was chosen as the ceramic support for the dual-phase membrane. This material has been extensively studied as electrolyte for solid oxide fuel cells [16]. It has also been shown to have high CO_2 permeance in the presence of molten carbonate at intermediate temperatures at high temperatures [13,17]. The objective of this work is to study the CO_2 permeation properties and stability of the SDC-carbonate dual-phase membrane under inert and simulated syngas conditions at high temperature and high pressure.

2. Experimental methods

2.1. Synthesis and characterization of ceramic-carbonate dual phase membranes

Samarium doped ceria (SDC) powder of composition $Ce_{0.8}Sm_{0.2}O_{2-x}$ was prepared by the citrate method previously described by Yin and Lin [18]. Stoichiometric amounts of metal nitrate precursors $Ce(NO_3)_3 \cdot 6H_2O$ (99.5%, Alfa Aesar) and $Sm(NO_3)_3 \cdot 6H_2O$ (99.9%, Alfa Aesar) were weighed out in a 0.05 mol basis and mixed with a 100% excess of citric acid (99.5%, Alfa Aesar). The precursors were dissolved in 1000 mL of de-ionized water and heated to 105 °C and covered for four hours to prevent evaporation and promote polymerization. Evaporation was then implemented by uncovering and heating the solution at 110 °C for 3–4 h. The resulting viscous solution was dried in a furnace (Thermolyne, 46100) at 110 °C for 24 h. Self-ignition of the dried gel was then performed at 400 °C to burn out the organic compounds. The resulting powder was then ground with a mortar and pestle to reduce the particle size. The powder was then calcined at 550 °C in air for 10 h with heating and cooling ramping rates of 10 °C min^{-1}. The calcined powder was again ground using a mortar and pestle. Approximately 3 g of powder was placed in a 30 mm stainless steel mold and pressed to 160 MPa for 5 min using a hydraulic press (Carver, Model #3853). The green disks were then sintered at 1100 °C for about 20 h with heating and cooling ramping rates of 2 °C min^{-1} resulting in porous SDC disk supports.

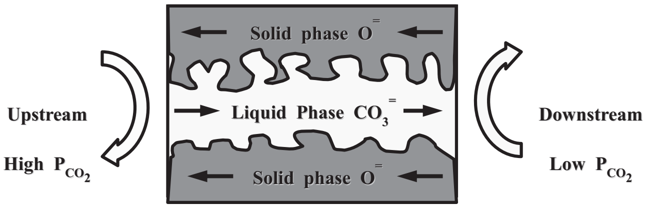

Fig. 1. Concept of ceramic-carbonate dual-phase membrane for CO_2 separation.

Synthesis of SDC-carbonate dual-phase membranes was achieved by direct infiltration of molten carbonate into the pores of sintered SDC support via the direct infiltration technique previously described by Chung et al. [4]. The carbonate powders Li_2CO_3 (99.2%, Fischer Scientific), Na_2CO_3 (99.9%, Fischer Scientific), and K_2CO_3 (99.8%, Fischer Scientific) were weighed out in a 42.5/32.5/25 mol% ratio, respectively, and heated to 550 °C in a furnace. This mixture has been previously studied and was chosen due to its relatively low melting point (397 °C) when compared to single or binary metal carbonates [4]. Porous ceramic supports were preheated above the molten carbonate mixture to prevent thermal shock prior to being lowered into contact with carbonate. Supports were left in contact with molten carbonate for 5–10 min to ensure complete infiltration via capillary force. The membrane was then lifted and slowly removed from the furnace and cooled. Residual carbonate on the membrane surface was removed using a SiC polishing paper.

The porosity of the porous ceramic supports was measured by the Archimedean method using liquid nitrogen [19,20]. Room temperature helium permeation was used to determine the average pore size of porous supports as well as verifying the gas tightness of dense ceramic and ceramic-carbonate dual-phase membranes. The phase structure of the SDC powder and membranes were characterized using X-ray diffraction (XRD) (Bruker, $CuK_{\alpha1}$) evaluated in the 2θ range of 20–80°. Scanning electron microscopy (SEM, Phillips, FEI XL-30) imaging was performed to confirm the porous nature of ceramic supports.

2.2. Carbon dioxide permeation measurements

For high temperature permeation experiments, two different permeation systems were used to measure CO_2 permeation fluxes at different system pressures. For atmospheric pressure permeation tests, a Probostat high temperature permeation system (Probostat, Norwegian Electro Ceramics AS) was used as previously described in the recent published work [14]. The central part of this setup is shown in Fig. 2. Using this system, a dense SDC-carbonate disk membrane and silver seal were placed on top