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Effects of support pore structure on carbon dioxide permeation of ceramic-carbonate dual-phase membranes



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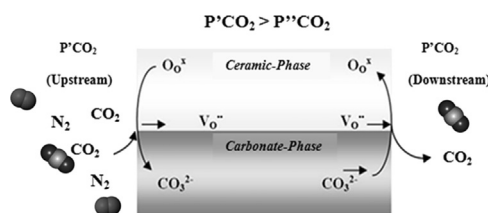
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HIGHLIGHTS

- Ceramic supports of various pore structures were prepared and characterized.
- A total conductance is defined with effective carbonate and ionic conductivities.
- CO₂ permeance of dual-phase membrane increases with increasing total conductance.
- Carbonate (porosity) or ceramic fraction to tortuosity ratio affects the total conductance.
- Microstructure of ceramic support is critical to enhancing CO₂ permeance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 10 July 2013

Received in revised form

13 September 2013

Accepted 16 September 2013

Available online 17 October 2013

Keywords:

CO₂ separation
Ceramic membrane
Ionic conductor
Dual-phase

ABSTRACT

Dual-phase membranes consisting of an ionic or mixed conducting ceramic phase and a molten carbonate phase are permeable only to carbon dioxide at high temperatures. This paper studies the effects of the pore structure of ceramic supports on carbon dioxide permeation properties of dual-phase membranes consisting of La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ} (LSCF) and eutectic Li₂CO₃–Na₂CO₃–K₂CO₃ carbonate phase. Porous LSCF supports with different pore structures were prepared by pressing LSCF powders followed by sintering at various temperatures. The porosity to tortuosity and solid fraction to tortuosity ratios for the porous LSCF supports were characterized by helium permeation and electrical conductivity measurements. The direct infiltration method allows complete filling of the ceramic support pores by the carbonate. CO₂ permeance of the dual-phase membranes increases, and after reaching a maximum, decreases with increasing support sintering temperature or support porosity (carbonate fraction). A total conductance in terms of the effective carbonate and ionic conductivities (intrinsic conductivity modified by the carbonate or solid fraction to tortuosity ratio) is introduced and used to explain experimental results. The results show that the CO₂ permeance of the dual-phase membrane is controlled not only by the intrinsic carbonate and oxygen ionic conductivities of the carbonate and ceramic phases, but also the carbonate or solid fraction to tortuosity ratio. Adjusting pore and solid microstructure of ceramic support is critical to maximize CO₂ permeance of the dual-phase membranes.

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1. Introduction

Emission of CO₂ produced by the combustion of fossil fuels to the atmosphere has been identified as the main contributor to the environmental problem of global warming (Meadowcroft and

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Langhelle, 2009; D-Figueroa et al., 2008; Pfeiffer, 2010). A potential CO₂ mitigation technique is the separation/capture of CO₂ from power plants and its use as a chemical feedstock for synthesis of chemicals (Choi et al., 2009; Busch et al., 2008; Orr, 2009). High temperature carbon dioxide perm-selective membranes offer potential for pre- and post-combustion CO₂ separation (Nair et al., 2009; Sherman et al., 2012; Anderson et al., 2012). Recently, we reported the development and carbon dioxide transport properties of a novel, dense dual-phase inorganic membrane that is able to separate CO₂ at intermediate and elevated temperatures (450–900 °C) (Chung et al., 2005; Anderson and Lin, 2010; Rui et al., 2012). The dual-phase membrane concept involves the CO₂ separation via the transport of carbonate ions (CO₃²⁻) across a membrane composed of a solid (ceramic or metallic) phase that serves as an anionically or electronically conductive support and an anionically conductive molten carbonate phase. In both cases, ceramic- and metallic-carbonate dual-phase membranes, the carbonate ions that are formed by intermediate electrochemical surface reactions are transported across the molten carbonate phase from the upstream to the downstream side of the membrane where the reverse reactions take place releasing molecular CO₂ to the gas phase.

As opposed to the metallic-carbonate membrane which requires of oxygen in the feed gas mixture (Chung et al., 2005; Xu et al., 2012), the ceramic-carbonate membrane includes an ionic conductive ceramic phase that can transport oxygen ions (O²⁻) which then reacts with CO₂ at the upstream membrane surface to form CO₃²⁻ as shown:



The CO₂ partial pressure gradient across the membrane serves as the driving force of the process. Based on this transport mechanism, this nonconventional inorganic membrane exhibits a potential to overcome the limitation of low selectivity of porous membranes at high temperatures (Anderson et al., 2012).

Rui et al. (2009) have proposed a mechanism and theoretical model that describes the high temperature permeation characteristics for the special case where CO₂ is able to transport through a dual-phase membrane with or without the presence of oxygen on the upstream side. This particular membrane consists of mixed ionic-electronic conducting oxide ceramic and molten carbonate phases. Fig. 1a shows a schematic of the CO₂ transport mechanism for the case where only a chemical gradient of CO₂ is considered; surface reaction (B) is shown. Moreover, Fig. 1b shows a schematic of the transport mechanism of CO₂/O₂; surface reactions (B and C) are considered as follows:



The dual-phase membrane reported by Anderson and Lin (2010) is an example of the aforementioned case, where the ceramic phase La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-δ} (LSCF) is a known ionic-electronic mixed conductor and the molten carbonate phase is an eutectic Li₂CO₃, Na₂CO₃ and K₂CO₃ mixture. The CO₂ permeation of membranes with different thicknesses was studied, and it was concluded that the permeation mechanism is controlled by oxygen ion conductivity in the solid skeleton of the LSCF support. A maximum CO₂ permeance of 4.77 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹ at 900 °C was observed for membranes with a thickness of 0.375 mm and a CO₂/Ar separation factor of 225.

Wade et al. (2011) reported the CO₂ separation properties of dual-phase thin membranes prepared by using yttria-stabilized zirconia or gadolinium-doped ceria as the ceramic ionic conducting phase and different molten carbonate mixtures. Membranes with thicknesses of 200–400 μm were fabricated via the tape casting technique.

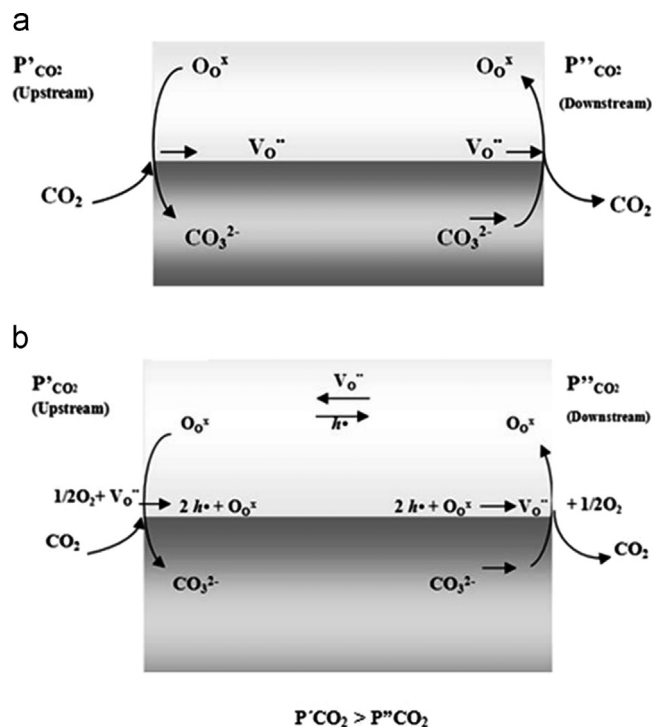


Fig. 1. Pictorial representation of the concept of the ceramic-carbonate dual-phase membrane for CO₂ separation: (a) considering only a chemical gradient of CO₂ and (b) considering oxygen in the upstream side that facilitates the transport mechanism. The darkened and lighter areas represent the molten carbonate and mixed ionic-electronic oxide phase, respectively.

Membranes were capable of separating CO₂ in the temperature range of 500–900 °C. The reported CO₂ permeance values at 750 °C were 2.0 × 10⁻⁸ and 3.0 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹ for the yttria-stabilized zirconia and gadolinium-doped ceria based membranes, respectively. More recently, Lin et al. (Rui et al., 2012) reported the fabrication of asymmetrically structured dual-phase membranes made of B_{1.5}Y_{0.3}Sm_{0.2}O₃ (BYS) and molten carbonate. Membranes with effective thicknesses of about 50 μm for the dense dual-phase membrane were fabricated by the direct infiltration of molten carbonate into the ceramic phase modified with γ-Al₂O₃. Due to the high ionic conductivity of the ceramic phase at intermediate temperatures and the thin membrane thickness in the micrometric scale, the BYS-carbonate membranes are capable of separating CO₂ in the temperature range of 500–650 °C. The reported CO₂ permeance at 650 °C was 1.1 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹.

The previously mentioned studies were focused on making the dual-phase membranes with various ceramic phases using different synthesis methods. Both modeling and experimental data reported so far have shown that CO₂ permeation of ceramic-carbonate membranes can be enhanced in a wide range of temperatures by reducing membrane thickness or by increasing the oxygen ionic conductivity of the ceramic phase that in fact has been identified as the limiting factor of the transport process.

The conductivities of SDC-carbonate composites are strongly affected by the porosity structure parameters of SDC phase including the tortuosity of pore channels and their specific interface area (Yin et al., 2013). It was also reported that samarium doped ceria (SDC)-carbonate ionic conductor composites are able to transport different ionic species through the interface formed between the molten carbonate and ceramic phase (Zhu et al., 2008; Zhao et al., 2012; Zhang et al., 2013), wherein microstructure features may be affected by the contribution of surfaces reactions other than those considered here (reactions B and C)

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