



Highly stable dual-phase $Y_{0.8}Ca_{0.2}Cr_{0.8}Co_{0.2}O_3-Sm_{0.2}Ce_{0.8}O_{1.9}$ ceramic composite membrane for oxygen separation



Kyung Joong Yoon ^{a,b}, Olga A. Marina ^{a,*}

^a Pacific Northwest National Laboratory, Richland, WA 99352, USA

^b Korea Institute of Science and Technology, Seoul 135-791, Republic of Korea

ARTICLE INFO

Article history:

Received 6 July 2015

Received in revised form

15 September 2015

Accepted 28 October 2015

Available online 31 October 2015

Keywords:

Dual-phase stable ceramic membrane

High-temperature oxygen separation

Oxygen permeability

High-purity oxygen production

Doped chromite–ceria composite

ABSTRACT

A highly stable ceramic composite membrane composed of Ca- and Co-doped yttrium chromite, $Y_{0.8}Ca_{0.2}Cr_{0.8}Co_{0.2}O_3$ (YCCC), and samaria-doped ceria, $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC), was demonstrated for oxygen separation. Homogeneously dispersed nano-scale composite powders were synthesized by a single-step combustion process based on the glycine–nitrate method. Dense composite membranes were achieved having submicron grain sizes and well-percolated electronic and ionic conduction pathways. Densification of the composite membrane was assisted by liquid phase sintering caused by cobalt-doping in yttrium chromite, and gas-tight membranes are fabricated at 1400 °C. The YCCC and SDC phases were chemically and thermo-mechanically compatible at both processing and operating temperatures. The composite membrane exhibited an oxygen permeation flux comparable to those of the state-of-the-art single-phase membrane materials and excellent stability in harsh operating conditions under a H_2-CO_2 environment for long-term operation, which suggests potential application in various combustion and fuel production processes.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

High-temperature oxygen transport membranes based on mixed ionic- and electronic-conducting (MIEC) ceramics are receiving increasing attention due to their potential applications for high-purity oxygen production, oxyfuel combustion, hydrogen/syngas production, coal gasification, and waste recovery [1,2]. Dense MIEC membranes exclusively allow the permeation of oxygen ions in the presence of an oxygen partial pressure gradient because the oxygen ionic flux is counterbalanced by the flux of electrons to form an internal short circuit. For practical applications, an MIEC membrane should be gas-tight, highly oxygen permeable, chemically stable and inexpensive.

Most candidate materials for use as ceramic MIEC membrane are either perovskite or fluorite structures [1]. Single-phase perovskite-type oxides such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ exhibit high oxygen permeability due to their high ambipolar conductivity, but practical applications have been limited because of their chemical and dimensional instability in a large oxygen chemical potential gradient, reactivity with CO_2 and relatively high thermal expansion behavior [3]. On the other hand, single-phase fluorite materials such as doped zirconia and doped ceria possess adequate

stability under the practical operating conditions, but oxygen permeability is low because of their low electronic conductivity [4,5].

Alternatively, dual-phase composite membranes composed of oxygen ion-conducting ceramics and electron-conducting noble metals have been proposed [6,7]. In this approach, the formation of the percolative paths for both phases is extremely important to obtain sufficient oxygen permeation flux [8], and in practice, at least 30–40 vol% of noble metal such as Pt, Pd or Ag is required to form a continuous path for electronic conduction [8,9], which is not acceptable from an economic perspective. To reduce the materials costs, all-ceramic composite membranes composed of a fluorite ionic conductor and a single- or double-perovskite electronic conductor, such as $Zr_{0.84}Y_{0.16}O_{1.92}-La_{0.8}Sr_{0.2}MnO_{3-\delta}$ [10,11], $Zr_{0.84}Y_{0.16}O_{1.92}-La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ [12,13], $Ce_{0.8}Gd_{0.2}O_{1.95}-La_{0.7}Sr_{0.3}MnO_{3-\delta}$ [14,15], $Ce_{0.9}Gd_{0.1}O_{1.95}-La_{0.6}Sr_{0.4}CoO_{3-\delta}$ [16], $Ce_{0.9}Gd_{0.1}O_{1.95}-La_{0.6}Sr_{0.4}FeO_{3-\delta}$ [16], $Ce_{0.9}Gd_{0.1}O_{2-\delta}-La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ [17], $Ce_{0.9}Gd_{0.1}O_{1.95}-Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [18,19], $Ce_{0.8}Sm_{0.2}O_{2-\delta}-La_{0.7}Ca_{0.3}CrO_{3-\delta}$ [20], $Ce_{0.8}Sm_{0.2}O_{2-\delta}-La_{0.8}Sr_{0.2}CrO_{3-\delta}$ [21,22], $Ce_{0.8}Sm_{0.2}O_{2-\delta}-Ba_{0.95}La_{0.05}Fe_{1-x}Zr_xO_{3-\delta}$ [23], $Ce_{0.85}Sm_{0.15}O_{1.925}-Sm_{0.6}Sr_{0.4}Al_{0.3}Fe_{0.7}O_{3-\delta}$ [24], $Ce_{0.8}Sm_{0.2}O_{2-\delta}-LnBaCo_{2}O_{5+\delta}$ ($Ln=La, Pr, Nd, Sm, \text{ and } Y$) [25–28], have been investigated. In all-ceramic composite membranes, the chemical interaction between the two phases readily leads to significant degradation at high temperatures, such that stability issues remain a concern as with single-phase perovskite materials [29]. Therefore, the development

* Corresponding author.

E-mail address: olga.marina@pnnl.gov (O.A. Marina).

of the dual-phase ceramic composite membrane with sufficient oxygen permeability and stability is highly desirable for commercial development of MIEC membrane technology.

Ca- and Co-doped yttrium chromite (YCCC), which has been developed as an interconnect material for solid oxide fuel cells (SOFCs), possesses excellent electronic conductivity, sinterability and stability over a wide range of oxygen partial pressure [30]. Samaria-doped ceria (SDC) is a well-known electrolyte material for SOFCs with high ionic conductivity and phase stability in both oxidizing and reducing environments [31]. The chemical compatibility of these two materials was also confirmed for application of the SOFC composite anode [32]. A composite of these two materials could possibly overcome the limitations of the conventional MIEC membrane materials, and may be a good candidate for use in oxygen separation membrane reactors operating under harsh conditions. In this work, the YCCC–SDC composite powder was synthesized by a single-step combustion process based on the glycine–nitrate combustion synthesis method, and dense MIEC composite membranes were fabricated via a low-temperature sintering process. The oxygen permeation characteristics and long-term stability were evaluated under various operating conditions, relative to practical oxygen separation from air and to partial oxidation of methane.

2. Experimental

YCCC–SDC composite powders were synthesized by a single-step combustion process based on the glycine–nitrate combustion method [33]. All of the nitrate precursors for the composite (yttrium, calcium, chromium, cobalt, samarium and cerium) were mixed in water with glycine according to the stoichiometric ratio (50 wt% of $Y_{0.8}Ca_{0.2}Cr_{0.8}Co_{0.2}O_3$ and 50 wt% of $Sm_{0.2}Ce_{0.8}O_{1.9}$) and co-burned in a single combustion step to form the dual phase composite. The obtained powder was calcined at 1100 °C for 2 h in air, and the formation of the composite phases was confirmed using X-ray diffraction (XRD) analysis. The powder morphology was investigated after calcination using transmission electron microscopy (TEM). Individual YCCC and SDC powders were synthesized and analyzed separately, as described elsewhere [30].

Composite disc membranes with various thicknesses (1.3, 1.9, and 2.4 mm) were fabricated by uniaxially pressing the composite powder at 35 MPa followed by isostatic pressing at 200 MPa and sintering at 1400 °C for 4 h in air. The area of the membrane was 1.98 cm². After sintering, the phase purity of the composite membrane was assessed using powder X-ray diffraction (XRD) of crushed samples. The relative density of sintered samples was measured using the Archimedes density measurement. Sintered samples were sectioned and impregnated with epoxy under vacuum. After the epoxy hardened, the samples were polished down to 0.25 μm and examined using scanning electron microscope (SEM). To investigate the effect of Co-doping in yttrium chromite on the sintering behavior of the composite membrane, a composite membrane without Co-doping ($Y_{0.8}Ca_{0.2}CrO_3$ (YCC)–SDC) was prepared using same procedure, and its cross-section was analyzed using SEM.

For oxygen permeation measurements, the membranes were mounted between two alumina tubes and sealed with gold o-rings at 950 °C by pressure loading. Gold o-rings were used instead of glass sealant to avoid chemical contamination on the membrane surface [34]. Air was supplied to the feed side at a flow rate of 30 ml min⁻¹, and various sweeping gases such as N₂, forming gas (3% H₂ balanced with N₂) and a mixture of 50% CO₂ and 50% forming gas were supplied to the permeate side of the membrane at the same flow rate. The oxygen partial pressure of the output gas from the permeate side was measured using a zirconia-based

oxygen sensor. The measurements were performed in the temperature range of 250–950 °C, and the oxygen flux was obtained based on the assumption that the increase in the total amount of oxygen in the permeate side from the baseline was entirely due to the oxygen ion permeation through the membrane. A long-term test was performed at 950 °C with a mixture of 50% CO₂ and 50% forming gas in the permeate side. YCCC–SDC phase stability after exposure to various gas environments was verified using XRD analysis.

3. Results and discussion

X-ray diffraction analyses of calcined powders, sintered compacts, and sintered membranes following extended exposure to H₂/CO₂ revealed the presence of two separate phases, Fig. 1. The two phases were identified as the perovskite YCCC and fluorite SDC. This result indicates that a composite of two separate phases can be prepared in one step using simple and cost-effective glycine–nitrate combustion method. The chemical compatibility between YCCC and SDC was verified by examining the XRD pattern of the composite powder obtained by crushing the sintered pellet at 1400 °C, also shown in Fig. 1. No indication of a reaction product or major peak shift was observed, implying that a processing temperature up to 1400 °C can be used for the densification of the membrane without causing problems associated with chemical interactions between the two phases. In addition, Fig. 1 contains XRD pattern obtained from the surface of the sample exposed to H₂ and CO₂ (50% forming gas + 50% CO₂) at 950 °C for over 350 h in a long-term test. There was no indication of phase decomposition or carbonate formation, showing the stability of the composite membrane in reducing and CO₂-containing environments for the conditions tested at 850 °C and above.

As shown in Fig. 2, the morphology of calcined composite powders was investigated by TEM after calcination at 1100 °C. The image reveals homogeneous mixture of the extremely fine particles with the primary particle size of 50–70 nm. Due to excellent powder characteristics such as small particle size and narrow size distribution, enhanced sinterability and microstructural control are expected in subsequent fabrication of the dense composite membranes. In particular, because the two phases exhibit extremely similar powder morphology, minimal hydrostatic tensile

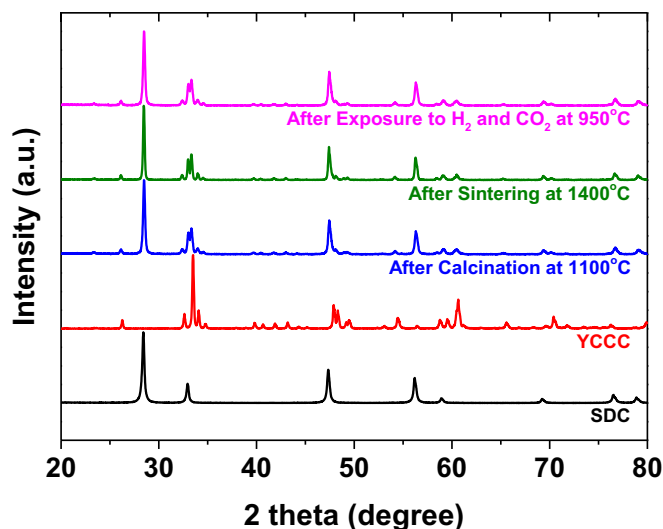


Fig. 1. XRD patterns of YCCC–SDC composite powder synthesized by the single-step glycine–nitrate process after calcination at 1100 °C in air, sintering at 1400 °C and exposure to H₂ and CO₂ for over 350 h at 950 °C. Patterns of pure YCCC and SDC powders are given as well.

Download English Version:

<https://daneshyari.com/en/article/632611>

Download Persian Version:

<https://daneshyari.com/article/632611>

[Daneshyari.com](https://daneshyari.com)