



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Oxygen-selective membranes integrated with oxy-fuel combustion

Wei Chen^a, Chu-sheng Chen^b, Henny J.M. Bouwmeester^{a,b}, Arian Nijmeijer^a, Louis Winnubst^{a,b,*}^a Inorganic Membranes, Mesa+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands^b CAS Key Laboratory of Advanced Materials for Energy Conversion and Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, PR China

ARTICLE INFO

Article history:

Received 4 December 2013

Received in revised form

8 March 2014

Accepted 23 March 2014

Available online 29 March 2014

Keywords:

Oxy-fuel

Perovskite

Membrane

CO₂ tolerance

ABSTRACT

The perovskite-type oxide SrCo_{0.8}Fe_{0.2}O_{3-δ} (SCF), a highly oxygen-permeable material, is restricted for application in the membrane-integrated oxy-fuel combustion process by its low tolerance to CO₂. In the present work, we found that the CO₂ tolerance of SCF is improved by increasing the oxygen partial pressure in the CO₂-containing gas. Long term oxygen permeation experiments, at 950 °C, show that mixing 5% of oxygen into the CO₂ sweep gas effectively prevents degradation of the SCF membrane. X-ray photoelectron spectroscopy indicates that the increase in CO₂ tolerance of SCF is caused by a decrease in basicity of the material with increasing oxygen partial pressure. Based on these experimental results, a modified oxy-fuel combustion process is proposed. Calculation of the required membrane area for operating a 50 MW coal-fired power plant showed that the modified process comprises a viable option.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Oxy-fuel combustion is a promising technique for CO₂ capture in a fossil fuel-fired power plant. In a typical oxy-fuel combustion process, pure oxygen instead of air is used for fuel combustion, resulting in a concentrated CO₂ gas stream, thus enabling efficient CO₂ capture. In most cases pure oxygen is separated from air via the cryogenic distillation or the pressure swing adsorption (PSA) process. Both processes are energy intensive, which limits further development of the oxy-fuel combustion technique [1,2]. It is proposed that oxygen can be produced by using mixed ionic-electronic conducting (MIEC) ceramic membranes, through which (neutral) oxygen transport at elevated temperatures (usually higher than 700 °C) [3,4]. A general scheme of this process is given in Fig. 1. The oxygen, as separated from air by the membrane, is carried by the sweep gas CO₂, while the CO₂/O₂ gas mixture is used to combust the fossil fuel. After combustion and purification, the exhaust gas mainly consists of CO₂ (> 95%). Part of the CO₂ is recycled as sweep gas and the rest is compressed for delivery and storage.

Most MIEC materials have the perovskite crystal structure and contain alkaline-earth elements like Ca, Sr or Ba. Due to the presence of these elements, a carbonation reaction tends to occur when these

membranes are exposed to a CO₂-containing atmosphere. This reaction results in the formation of an alkaline-earth carbonate layer on the membrane surface, which is impermeable for oxygen, resulting in a decline in oxygen flux or even to a non-permeating membrane. For example, SrCo_{0.8}Fe_{0.2}O_{3-δ} (SCF), a highly oxygen-permeable material, shows a decrease in oxygen flux to almost zero within 100 h when using CO₂ as sweep gas [5]. In order to increase the CO₂ tolerance of SCF membranes, Sr²⁺ was partially substituted with La³⁺ [6], or Co/Fe with Ti⁴⁺, Zr⁴⁺, Ta⁵⁺ or Nb⁵⁺ [7,8]. However, this improvement in CO₂ tolerance was at the expense of a decrease in oxygen flux [9].

Besides partial substitution, there are other parameters that affect the CO₂ tolerance of SCF, for example, temperature and CO₂ partial pressure (*p*CO₂). Yi et al. [10] found that SCF is more stable at higher temperature and lower *p*CO₂ (balanced with helium), and suggested SCF membranes should be operated above 900 °C. In the present study we examined another possible parameter: the oxygen partial pressure (*p*O₂), which has not been reported before to the best of our knowledge, as a way to improve the CO₂ tolerance of alkaline-earth containing perovskite materials. In this study thermal-gravimetric analysis (TGA) was used to investigate the effect of *p*O₂ on the stability of the SCF perovskite system in a CO₂-containing atmosphere. X-ray photoelectron spectroscopy (XPS) was used to examine the oxygen bonding energy of SCF at different oxygen partial pressures. Oxygen permeation experiments were performed to test the CO₂ tolerance of SCF membranes under operating conditions by adding 0% or 5% of oxygen to the sweep

* Corresponding author at: Inorganic Membranes, Mesa+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands.
E-mail address: a.j.a.winnubst@utwente.nl (L. Winnubst).

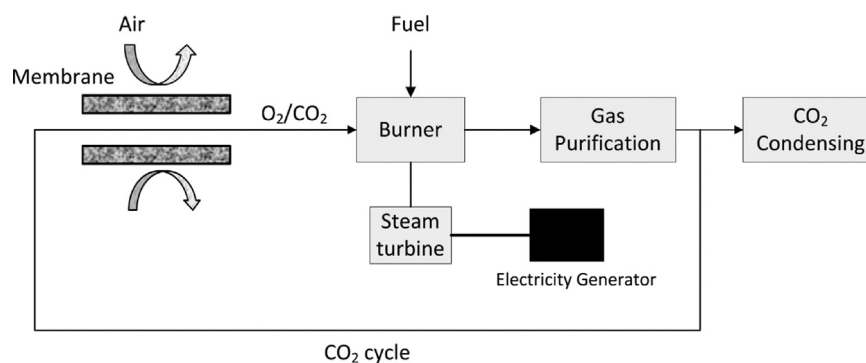


Fig. 1. Scheme for the membrane integrated oxy-fuel combustion process.

gas (CO₂). Finally, we propose a modified oxy-fuel combustion process and estimated the SCF membrane area needed in a combustion process for a 50 MW coal-fired power plant.

2. Experimental procedure and methodology

2.1. Sample preparation

SrCo_{0.8}Fe_{0.2}O_{3-δ} (SCF) was synthesized using an EDTA complexation/pyrolysis process. Metal nitrates were dissolved at a stoichiometric ratio in demineralized water under stirring. EDTA, dissolved in ammonium hydroxide, was added for chelating and after several minutes citric acid was added as well. The molar ratio of total metal ions: citric acid: EDTA was 1.0:1.5:1.0. The pH of the solution was adjusted to 6 by adding ammonium hydroxide. Subsequently NH₄NO₃ was added as an ignition aid at an amount of 100 g NH₄NO₃ per 0.1 mol of metal ions. The final solution was heated at 120–150 °C under stirring to evaporate water until the system changed into a viscous gel, which was transferred to a stainless steel vessel and heated on a hot plate at a temperature of around 500 °C, while a vigorous combustion took place, resulting in a fluffy powder. The powder was collected and calcined at 950 °C for 5 h at a heating and cooling rate of 3 °C/min. The calcined powders were uniaxially pressed at 4 MPa into disk-shaped membranes, subsequently cold isostatically pressed at 400 MPa for 6 min, and sintered in ambient air at 1200 °C for 10 h at a heating rate of 3 °C/min and a cooling rate of 2 °C/min.

2.2. Thermal-gravimetric analysis (TGA)

Isothermal gravimetric analyses were carried out on a Netzsch TG 449 F3 Jupiter[®]. About 45 mg of SCF powder was weighed in an alumina crucible and placed in the TGA setup. The system was heated (10 °C/min) to the desired temperature, in the range 900–1000 °C, in a flowing (120 ml/min) O₂/N₂ mixture at four different oxygen partial pressures (*p*O₂), namely 10⁻⁴, 0.05, 0.1 and 0.2 bar. The system was held at this temperature for 1 h to attain equilibrium. Next, the purge gas was switched to a mixture of O₂/N₂/67% CO₂ (flow rate 120 ml/min), keeping the oxygen partial pressure (and thus the oxygen flow rate) in the gas mixture identical as before switching (so respectively 10⁻⁴, 0.05, 0.1 and 0.2 bar). After 5 h, the system was cooled down at 20 °C/min in the same purge gas. All TGA data were processed with a correction file of a blank crucible using the same temperature program, to exclude background data of the equipment.

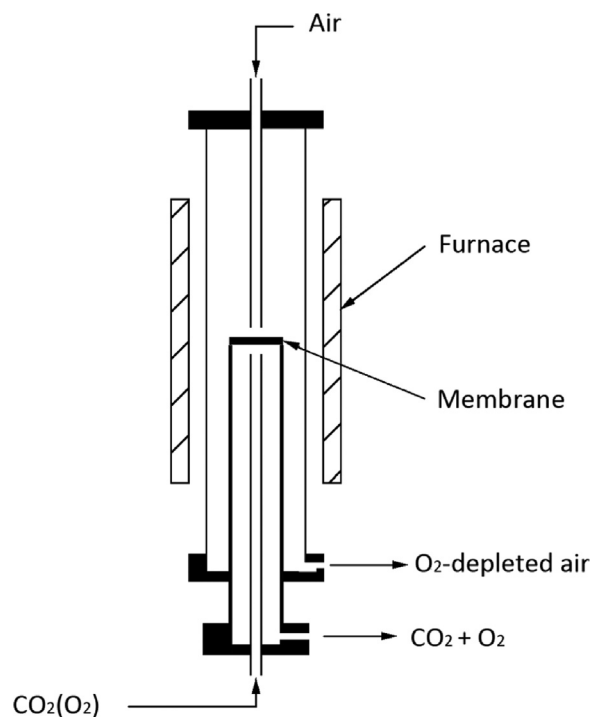


Fig. 2. Schematic diagram of the high temperature permeation setup.

2.3. X-ray photoelectron spectroscopy analysis

For X-ray photoelectron spectroscopy (XPS: ESCALAB MK II, VG equipment) analysis SCF bars (8 mm × 4 mm × 3 mm) were prepared using the same procedure as for the disk-shaped membranes. After sintering and polishing to the desired dimensions, the samples were annealed in nitrogen (*p*O₂ = 10⁻⁴ bar) or oxygen (*p*O₂ = 1.0 bar) at 950 °C for 20 h and quenched to room temperature within a few seconds. Afterwards, the bars were fractured and only the center part of the cross section was analyzed by XPS using an X-ray beam size of 250 μm and a step size of 0.05 eV.

2.4. Oxygen permeation measurements

The experimental setup for oxygen permeation measurements is schematically shown in Fig. 2. Disk-shaped membranes with a diameter of 15 mm and a relative density > 90% were polished to a thickness of 1 mm and ultrasonically cleaned in ethanol. The membranes were sealed to one end of a quartz tube (diameter 12 mm) using gold paste and a sealing temperature of 1000 °C. After sealing, the temperature was lowered to 950 °C, and air was

Download English Version:

<https://daneshyari.com/en/article/633607>

Download Persian Version:

<https://daneshyari.com/article/633607>

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