



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/hydro](http://www.elsevier.com/locate/hydro)

# Hebb-Wagner polarization assessment of enhanced oxygen permeability for surface modified oxygen transport membranes

Xuejiao Liu <sup>a,b</sup>, Hao Wu <sup>a</sup>, Zhenyu He <sup>c</sup>, Jun Gao <sup>a,b</sup>, Xie Meng <sup>a</sup>, Ting Luo <sup>a</sup>, Chusheng Chen <sup>c</sup>, Zhongliang Zhan <sup>a,\*</sup>

<sup>a</sup> CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS), 1295 Dingxi Road, Shanghai 200050, PR China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, PR China

<sup>c</sup> CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science & Engineering, University of Science & Technology of China (USTC), Hefei 230026, PR China

## ARTICLE INFO

### Article history:

Received 18 January 2017  
 Received in revised form  
 7 March 2017  
 Accepted 29 March 2017  
 Available online xxx

### Keywords:

Oxygen transport membranes  
 Oxygen permeability  
 Surface modification  
 Nanostructures  
 Catalysts

## ABSTRACT

Tri-layered “porous | dense | porous”  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ - $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{2-\delta}$  (LSCrF-YSZ) oxygen transport membranes (OTMs) were fabricated and permeation resistances from oxygen reduction and evolution reactions were determined by using Hebb-Wagner polarization method after introducing additional electron-blocking YSZ thin layers within the dense LSCrF-YSZ layers. Adding nano-scale catalysts, i.e.  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCoF) on air side and  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9-\delta}/\text{Ni}$  (SDC/Ni) on  $\text{CH}_4$  side, into the porous LSCrF-YSZ layers yielded substantially reduced interfacial polarization resistances, and thereby allowed for high oxygen permeability at reduced temperatures under the air/ $\text{CH}_4$  gradient, e.g., 1.1 and 4.3  $\text{ml cm}^{-2} \text{min}^{-1}$  at 650 and 800 °C, respectively. Analysis of the impedance spectra suggest that the oxygen reduction kinetics on air side was probably limited by charge transfer reaction at  $T \geq 750$  °C and surface oxygen exchange at  $T \leq 700$  °C. Meanwhile, oxygen evolution reactions on  $\text{CH}_4$  side dominated the total resistances to oxygen permeation through the tri-layered OTMs.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

The last decade has witnessed continuously increased interest in oxygen transport membranes (OTMs) due to their potential applications in oxygen separation [1],  $\text{CO}_2$  capture and storage [2,3], partial oxidation of methane to syngas [4,5], selective oxidation of light hydrocarbons [6], hydrogen production [7], and direct decomposition of  $\text{NO}_x$  [8]. Such an important versatility stems from the unique feature of the

membranes to simultaneously transport oxide ions and electrons that allows for selective separation of oxygen from air at elevated temperatures under large oxygen partial pressure gradients [1]. Owing to their high electrical conductivities, superior oxygen diffusivities and low manufacturing costs, single phase and oxygen-deficient perovskite oxides ( $\text{ABO}_{3-\delta}$ ) have become the state-of-the-art OTM materials, especially those with Sr/Ba on the A-site and Co/Fe on the B-site such as  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  [9],  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  [10], and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  [11,12]. For instances, 1.8 mm thick

\* Corresponding author.

E-mail address: [zzhan@mail.sic.ac.cn](mailto:zzhan@mail.sic.ac.cn) (Z. Zhan).

<http://dx.doi.org/10.1016/j.ijhydene.2017.03.206>

0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> membranes produced an oxygen permeability flux of  $\approx 1.4 \text{ ml cm}^{-2} \text{ min}^{-1}$  under the gradient of air/He at 950 °C [11]. Nonetheless, chemical and mechanic stability of these perovskite oxides has remained problematic during their long-term operation at the relevant operating conditions, particularly in the reducing atmospheres or CO<sub>2</sub>/SO<sub>2</sub>/H<sub>2</sub>O-containing atmospheres. Coating thin and dense protective layers of doped ceria on these perovskite membranes enhanced their resistances against the reducing or corrosive gases, with the nominal oxygen permeation flux only slightly reduced [13]. Partial substitution of the reducible ions (e.g., Co and Fe) with valence-constant cations (such as Zr<sup>4+</sup>, Nb<sup>5+</sup>, Ga<sup>3+</sup> and Al<sup>3+</sup>) also helped improve their stability, but inevitably resulted in substantially smaller permeation fluxes [14].

Another strategy to address the stability issues is to design dual-phase composite membranes via appropriate choice of the constituting oxide ionic conductors and electronic conductors that provide independent pathways to transport oxide ions and electrons [2,3,15]. A number of dual-phase membranes, such as La<sub>0.8</sub>Ca<sub>0.2</sub>CrO<sub>3-δ</sub>-Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2-δ</sub> [16], Sm<sub>0.6</sub>Sr<sub>0.4</sub>Al<sub>0.3</sub>Fe<sub>0.7</sub>O<sub>3-δ</sub>-Ce<sub>0.85</sub>Sm<sub>0.15</sub>O<sub>2-δ</sub> [17], Y<sub>0.8</sub>Ca<sub>0.2</sub>Cr<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3-δ</sub>-Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>2-δ</sub> [18], La<sub>0.8</sub>Sr<sub>0.2</sub>Cr<sub>0.5</sub>Fe<sub>0.5</sub>O<sub>3-δ</sub>-Zr<sub>0.84</sub>Y<sub>0.16</sub>O<sub>2-δ</sub> (LSCrF-YSZ) [2,4,19,20], have demonstrated substantially better mechanic and chemical stability than the common single-phase OTMs under the harsh or reducing environments. On the other hand, operation at relatively high temperatures (typically  $T \geq 900 \text{ °C}$ ) was required for these dual-phase OTMs to achieve acceptable oxygen permeation fluxes ( $J_{O_2}$ ) due to their poor electronic and oxide-ionic conductivities [2]. Nevertheless, such high operating temperature may introduce difficult challenges related to seals and long-term durability. Reducing the operating temperature below 800 °C can help mitigate these issues, but inevitably produces substantially smaller  $J_{O_2}$  values due to exponentially decreased permeation kinetics. Up to date, very few of these dual-phase oxygen transport membranes could meet the targeted  $J_{O_2}$  values of 1–10 ml cm<sup>-2</sup> min<sup>-1</sup> at reduced temperatures [1].

Here, we report a nanostructured architecture for oxygen transport membranes that allowed for high oxygen permeability at reduced temperatures under the air/CH<sub>4</sub> gradient. The new architecture featured thin dense LSCrF-YSZ permeation layers sandwiched between two porous LSCrF-YSZ layers, providing low resistances to bulk oxygen transport. Surface oxygen exchange resistances were minimized by coating the pore walls of LSCrF-YSZ scaffolds with nano-scale La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> (LSCoF) on the air sides and with Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9-δ</sub>/Ni (SDC/Ni) on the methane sides. By introducing additional electron-blocking YSZ thin films within the permeation layers, the permeation resistances from bulk oxygen transport and interfacial oxygen reduction or evolution reactions were for the first time measured by using the Hebb-Wagner polarization method.

The present unique OTM architecture, i.e., nano-LSCoF@LSCrF-YSZ | LSCrF-YSZ | nano-SDC/Ni@LSCrF-YSZ, was designed by taking account of the following observations:

- (1) LSCrF and YSZ were chemically and structurally stable in both oxidizing and reducing environments with acceptable electronic and ionic conductivities at

700–900 °C [20], respectively. Based upon the thermodynamic calculations, the decomposition oxygen partial pressure of LSCrF (e.g.,  $6.3 \times 10^{-28} \text{ atm}$  at 950 °C) decreased rapidly with decreasing temperature, indicating substantially better stability at reduced temperatures [21].

- (2) The rigid “porous | dense | porous” tri-layer ceramic architecture has been actively under investigation in solid oxide fuel cells (SOFCs), which can be easily scaled up with the pore structure tailored by selecting different pore formers [22,23]. Better connectivity of the YSZ phases within the co-sintered structures facilitated oxygen transport across the “porous | dense” interfaces. Additionally, the porous layers increased the densities of triple-phase boundaries (i.e., the contiguous contact of electronic, ionic and gas phases), where the oxygen reduction or evolution reactions occurred [23].
- (3) LSCoF oxides were highly active for oxygen reduction reactions, and have been widely explored as the SOFC cathodes [24].
- (4) SDC/Ni composites can catalyze direct methane oxidation in SOFCs as well as methane reforming reactions [25].

## Experimental

### Fabrication of “porous | dense | porous” LSCrF-YSZ structures

The OTM architecture was based upon tri-layered structures of “porous | dense | porous” LSCrF-YSZ, which were fabricated using the tape casting, tape lamination and co-firing techniques. LSCrF powders (Ruier Powder Material Corporation, China), (ZrO<sub>2</sub>)<sub>0.92</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>0.08</sub> (Tosoh Corporation, Japan) and graphite (Shanshan Technology, China) were used as the starting materials. The tape casting slurry was xylene based and consisted of appropriate amounts of dispersing agents, binders and plasticizers in addition to ceramic powders. Graphite was added as the fugitive material at 40 wt% relative to the LSCrF-YSZ ceramic powders for the two porous layers. The weight ration of LSCrF to YSZ was 58/42. The laminated green tapes were co-fired at 1410 °C for 4 h to produce the final tri-layered structures.

### Fabrication of nanostructured OTMs

Nano-scale catalysts were coated inside the pore walls of the porous LSCrF-YSZ scaffolds: Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub>/NOi (SDC/NiO) on the fuel side and La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> (LSCoF) on the air side. The mixed nitrate solutions of Ni(NO<sub>3</sub>)<sub>2</sub>, Sm(NO<sub>3</sub>)<sub>3</sub> and Ce(NO<sub>3</sub>)<sub>3</sub> at stoichiometric ratios (SDC:Ni = 80:20 wt) were impregnated into one of the porous LSCrF-YSZ scaffolds while the opposite scaffolds were impregnated with an aqueous solution containing La(NO<sub>3</sub>)<sub>3</sub>, Sr(NO<sub>3</sub>)<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, and citric acid at molar ratios of 0.6:0.4:0.2:0.8:3, followed by calcinations at 850 °C in air for 2 h. Multiple impregnation/firing cycles were usually used in order to introduce a sufficient amount of catalysts into the LSCrF-YSZ scaffolds.

Download English Version:

<https://daneshyari.com/en/article/5146204>

Download Persian Version:

<https://daneshyari.com/article/5146204>

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