



Highly oxygen-permeable and CO₂-stable Ce_{0.8}Sm_{0.2}O_{2-δ}-SrCo_{0.9}Nb_{0.1}O_{3-δ} dual-phase membrane for oxygen separation

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ABSTRACT

Dual-phase composite oxide 60 wt% Ce_{0.8}Sm_{0.2}O_{2-δ}-40 wt% SrCo_{0.9}Nb_{0.1}O_{3-δ} (60SDC-40SCN) which exhibits high oxygen permeability and good CO₂ tolerance was developed. X-ray diffraction (XRD) patterns and dense surface topography observed by scanning electron microscopy (SEM) revealed a good compatibility of the two oxides. A high oxygen permeation flux of 1.54 mL min⁻¹ cm⁻² through the as-prepared dual-phase membrane (0.8 mm in thickness) was obtained under the gradient of air/He at 1223 K. *In situ* high-temperature X-ray diffraction demonstrated that SDC and SCN in 60SDC-40SCN membrane could retain their original phase structure from room temperature to 1223 K in CO₂-containing atmosphere. The oxygen permeation fluxes of 60SDC-40SCN membrane showed a good reversibility when switching the sweep gas between CO₂ and He. Comparing with single-phase SCN membrane, oxygen permeation flux of dual-phase 60SDC-40SCN membrane was more than twice when pure CO₂ acted as the sweep gas, and the oxygen permeation flux could remain stable for 120 h. All the experimental results imply that dual-phase 60SDC-40SCN membrane has a great potential in oxy-fuel combustion process.

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1. Introduction

With greenhouse gases build-up in the atmosphere, global warming has become a public concern. Among all the sources of greenhouse gases emission, combustion of fossil fuel or coal in power plants is a primary polluter of carbon dioxide which needs to be addressed urgently. As one of the most promising CO₂ capture technologies, oxy-fuel process has been carried out to promote and optimize the combustion of fossil fuel and coal [1–3]. A typical oxy-fuel combustion process uses pure oxygen instead of air for fuel combustion, resulting in a concentrated CO₂ gas stream for the subsequently high-efficiency CO₂ capture to realize emission reduction of greenhouse gases [4,5]. Nevertheless, oxygen supply come from conventional air separation technologies on the basis of cryogenic distillation and pressure swing adsorption require large scale energetic and economic costs. Alternatively, mixed ionic electronic conducting (MIEC) oxygen permeation membrane process, which can be integrated with the combustion process providing pure oxygen in a lower implementation costs, may have great potential

for oxygen separation [6,7]. Furthermore, because MIEC oxygen permeation membranes allow 100% oxygen selectivity [8], the emissions of NO_x can also be reduced [9] and carbon capture and sequestration process can be implemented during combustion [10].

Over the past few decades, a large amount of research activities have been focused on MIEC oxides development, and a series of state-of-the-art materials with good oxygen permeation performance were developed [11]. Among them, Co-containing perovskite-type oxides, such as Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) [12], SrCo_{0.8}Fe_{0.2}O_{3-δ} [13], which exhibit very high oxygen permeability, were considered as the most promising membrane materials for industrialization. Unfortunately, their poor stability in CO₂ or SO₂ atmosphere limits their practical applications in oxygen permeation membranes. This attributes to the alkaline earth metal elements (such as Ba²⁺ and Sr²⁺ which have large ionic radii) on A site show susceptible to the acidic gas and easily occur reactions forming carbonates and sulfates [14,15]. In addition, the variation in the valence of cobalt makes it behave imperfectly in terms of structure stability [16,17]. Alternatively, dual-phase composite oxides which allow ions and electrons transport in different phases show superiority in stable oxygen permeability under CO₂ atmosphere [18], such as NiFe₂O₄-Ce_{0.8}Tb_{0.2}O_{2-δ} [9], Nd_{0.6}Sr_{0.4}FeO_{3-δ}-Ce_{0.9}Nd_{0.1}O_{2-δ} [19], Ce_{0.9}Gd_{0.1}O_{2-δ}-δ-NiFe₂O₄ [20], Ce_{0.8}Gd_{0.2}O_{2-δ}-δ-La_{0.7}Sr_{0.3}MnO_{3-δ} [21], Ce_{0.8}Sm_{0.2}O_{3-δ}-δ-La_{0.8}Sr_{0.2}CrO_{3-δ} [22] and Zr_{0.84}Y_{0.16}O_{1.92}-La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-δ} [23].

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However, on account of the inefficient electronic and oxygen ions transport [7,24], the poor oxygen permeability of most dual-phase membranes cannot meet the industrial requirements.

Because single-phase mixed conducting oxides with highly oxygen-permeable, such as Co-containing oxides, still play an irreplaceable role in future practical application, how to improve stability of these materials is an important issue demanding prompt solution. According to the design strategy of dual-phase oxygen permeation membrane mentioned above, we report a method that doping fluorite-type oxides into the Co-containing composites to achieve highly oxygen permeable and CO₂ stable dual-phase membrane materials. Here we select Ce_{0.8}Sm_{0.2}O_{2-δ} (SDC) which has fast oxygen ions conductivity and good performance in chemical durability as oxygen ion transport materials. And perovskite oxide SrCo_{0.9}Nb_{0.1}O_{3-δ} which has good structure stability [13] and high oxygen permeability [25] act as the oxygen ion and electronic conductors. In this work, phase structures and surface morphology of the as-prepared dual-phase membranes were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM) respectively. To test the oxygen permeability of the dual-phase membranes, the oxygen permeation fluxes as functions of SDC/SCN mass ratios and membrane thickness were investigated. In order to examine the CO₂ tolerance of the dual-phase membrane, the oxygen permeability, the phase structure change and chemical stability were investigated systematically under different CO₂ atmospheres.

2. Experiment

2.1. Preparation of SDC and SCN powders

The powder of SDC was synthesized via a combined EDTA-citrate complexing sol-gel method [26]. Briefly, the required amounts of analytic grades metal nitrates of Sm (NO₃)₃ and Ce (NO₃)₃ were dissolved in aqueous solution, followed by the addition of EDTA, the molar ratio of citric acid:EDTA:total metal ions was 1.5:1:1. The pH value of the solution was adjusted in the range of 6–8 by the addition of ammonium hydroxide. Under the condition of 363 K heating and stirring, the gel was obtained with the evaporating water. The gel was pre-fired in the air at 523 K to remove organic compounds and further calcined at 1073 K for 5 h under air atmosphere to obtain desired structural composition.

SrCo_{0.9}Nb_{0.1}O_{3-δ} powder was fabricated by the conventional solid-state reaction techniques. The required stoichiometric amounts of SrCO₃, Co₂O₃ and Nb₂O₅ were mixed in the ethanol solution and then ball milled for 24 h. After the solvent evaporated, the mixed oxides were calcined in muffle furnace at 1223 K for 5 h with heating and cooling rates of 5 K min⁻¹. The sintered SCN powder was grinded and sieved (300 meshes) to prepare the dual-phase composite oxides and membranes.

The dual-phase composite oxides 50 wt% SDC-50 wt% SCN, 60 wt% SDC-40 wt% SCN, 75 wt% SDC-25 wt% SCN were mixed in a agate jar and ball milled for 10 h to prepare homogeneous dual-phase composite oxides.

2.2. Membrane preparation and characterization

The dual-phase composites were pressed into disks under a pressure of ~200 MPa. The green disks were sintered at 1373 K for 10 h. The crystal phase structures of the SCN, SDC and different compositions of dual-phase membranes were characterized by X-ray diffraction (XRD, Bruker, model D8 Advance) with Cu Kα radiation. The variation of crystal structures with temperature were characterized by *in situ* XRD equipped with a high temperature attachment (*in situ* HTXRD, Philips, X'Pert Pro). The samples were tested in air and 50 vol% N₂/50 vol% CO₂ atmosphere from 298 K to 1273 K with a heating rate of 5 K min⁻¹ and each temperature point was held for 30 min for thermal equilibrium before diffraction data collection. All of the diffraction patterns were collected by step scanning at an increment of 0.05° in the range 20° ≤ 2θ ≤ 80°. The morphology

and micro-structure of the single and dual-phase membranes were examined by environmental scanning electron microscopy (SEM, Hitachi S-4800, Japan). A gas-tight test was conducted on the sintered asymmetric membrane using nitrogen at room temperature.

2.3. Oxygen permeation flux measurement

Oxygen permeation fluxes through the single-phase and dual-phase membranes were measured by a high-temperature oxygen permeation device which can be seen in our previous work [27]. A disk membrane with effective diameter of 7.5 mm was sealed on the end of an alumina tubes with silver adhesives. Temperatures of the oxygen permeation measurement device were monitored by a programmable temperature controller (AI-708PA, Yudian, China). Flow rates of the feed and sweep gas were controlled by mass flow controllers (D07-19B, Sevenstar, China). The gaseous mixture were analyzed by an On-Line gas chromatograph (GC-8A, Shimadzu, Japan), which equipped with a 2 m 5 A molecular sieve with helium (He) as the carrier gas. The leakage of the oxygen due to the defective sealing at high temperatures was <5% of the total oxygen permeation flux during all the experiments. The computational methods of oxygen permeation flux have also illustrated in our previous works [28].

3. Results and discussion

3.1. Phase and microstructure

The XRD patterns of dual-phase membranes sintered at 1373 K for 5 h are shown in the Fig. 1. As references, single-phase SDC and SCN are also included. For SDC pattern, the diffraction peaks at the respective 2-theta angles of 28.42° (111), 32.96° (200), 47.28° (220), 56.12° (311), 58.86° (222) and 76.42° (331) matches the fluorite structure. And for SCN, the 2-theta angles of 32.72° (110), 40.5° (111), 47.06° (200), 58.42° (211), 68.44° (220) 77.86° (310) corresponding to the perovskite structure. No additional phase resulting from undesirable reaction can be found from the diffraction peaks of the 60SDC-40SCN dual-phase at the room temperature, suggesting that the sintered membrane consists of only SDC and SCN phases. The patterns of the 50SDC-50SCN and 75SDC-25SCN are also depicted, same as the 60SDC-40SCN, no significant formation of impure phases can be found, revealing the stable co-existence of SDC and SCN in dual-phase membrane.

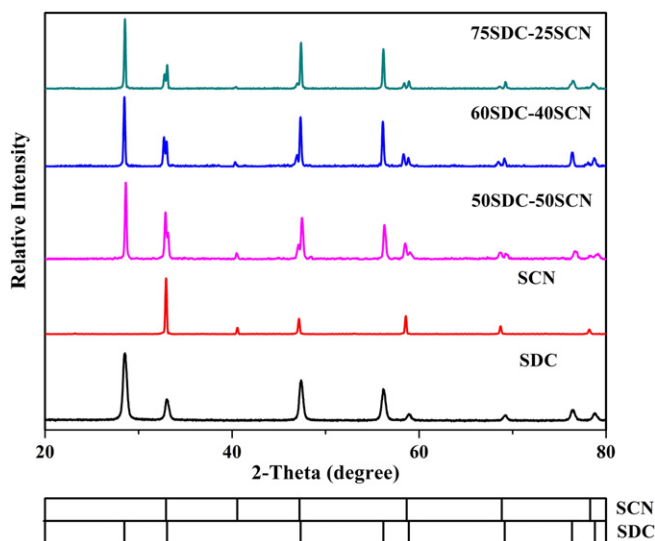


Fig. 1. XRD patterns of the SCN, SDC and SDC-SCN membranes. 50SDC-50SCN, 60SDC-40SCN and 75SDC-25SCN denote 50 wt% Ce_{0.8}Sm_{0.2}O_{3-δ}-50 wt% SrCo_{0.9}Nb_{0.1}O_{3-δ}, 60 wt% Ce_{0.8}Sm_{0.2}O_{3-δ}-40 wt% SrCo_{0.9}Nb_{0.1}O_{3-δ} and 75 wt% Ce_{0.8}Sm_{0.2}O_{3-δ}-25 wt% SrCo_{0.9}Nb_{0.1}O_{3-δ} respectively.

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