



CO₂-tolerant mixed conducting oxide for catalytic membrane reactor

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ABSTRACT

A new kind of La_{0.85}Ce_{0.1}Ga_{0.3}Fe_{0.65}Al_{0.05}O_{3-δ} (LCGFA) mixed conducting oxide was prepared by solid-state reaction method. The crystal structure, chemical stability, thermal expansion behavior, mechanical strength and oxygen permeability of this oxide were investigated. LCGFA powder was multiphase and mainly composed of perovskite phase and CeO₂ phase. After annealing in 20 vol.% CO₂ + He for 100 h or in 5 vol.% H₂ + He for 25 h at 900 °C, LCGFA powders still maintained full perovskite structure. LCGFA oxide showed very low chemical expansion and the average thermal expansion coefficients were 10.29(8), 10.68(8) and 10.73(6) × 10⁻⁶ °C⁻¹ in the temperature ranges of 200–1000 °C in air, nitrogen and carbon dioxide atmospheres, respectively. The three-point bending strength of the LCGFA sample reached 110 ± 5 MPa. At 950 °C, the oxygen flux of the supported LCGFA membrane with 200 μm membrane layer was 6.54(5) × 10⁻⁷ mol cm⁻² s⁻¹. The degradation of the membrane performances on either temperature cycling or during prolonged isothermal tests was found almost negligible.

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1. Introduction

During the past two decades, mixed ionic–electronic conducting (MIEC) materials have received great interest because of their potential applications in separation of oxygen from air [1–3], preparation of electrodes for solid oxide fuel cells (SOFCs) [4,5], and construction of membrane reactors for partial oxidation of methane to syngas [6–10] and oxidative coupling of hydrocarbon to value-added products [11,12]. The main advantage of the MIEC membrane reactor is that air instead of oxygen can be used as the oxygen source, which avoids the expensive separation of the nitrogen either before or after the reaction. Further more, the gradual introduction of oxygen reduce the contact with the partially oxidized products, which enhances the yield of the desired products. The formidable problem hinders the practical application of the MIEC membrane reactor is that the membrane has limited thermal and chemical stability at high temperatures and under a large oxygen gradient with one side of the membrane exposed to oxidizing atmosphere and the other side to the reducing atmosphere. Recently, several ways have been proposed to improve the structural stability of MIEC membrane materials, such as substituting A and/or B-site cations with more stable metal ions [3,13,14] and introducing certain amounts of second phase oxides into the perovskite-type oxides [2,15]. Wu et al. [15] reported that 3 wt.% Al₂O₃-doped SrCo_{0.8}Fe_{0.2}O_{3-δ} membrane successfully operated in the partial oxidation of methane

(POM) reaction for more than 500 h without fracture. Sammels and co-workers [16] developed a series of stable La_{2-x}Sr_xGa_yFe_{2-y}O_{5+δ} membrane materials, which could be operated in the POM reaction for 1000 h.

However, besides the reducing atmosphere, small amount of CO₂ is contained in natural gas as well it is a by-product of the syngas production. So, CO₂ atmosphere also needs to be considered in the MIEC membrane reactor. Unfortunately, CO₂ is a sensitive gas to most of the MIEC materials [17–24] because of the existence of alkaline-earth elements in these materials. Cheng and co-workers [19] demonstrated that the performance of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) cathode could be deteriorated by even small amount of CO₂ owing to its reaction with alkaline-earth elements resulting in the formation of Ba and Sr carbonates. Arnold et al. [20] found that the surface of BSCF membrane decomposed to be two different carbonate phases with the maximum depth of 40–50 μm when the membrane was exposed to CO₂ for about 72 h. Tong et al. [21] reported that the oxygen permeation flux of Ba(Co_{0.4}Fe_{0.6-x}Zr_x)O_{3-δ} membranes significantly decreased when CO₂ was introduced into the sweep gas. In our previous work [22,23], we proposed a novel MIEC membrane reactor, which coupled the thermal decomposition of carbon dioxide (TDCD) with the POM reaction. In this membrane reactor, TDCD took place in one side of the membrane and the POM occurred simultaneously in the other side of the membrane, or more clearly, methane reacted with oxygen, which was permeated through the membrane from the CO₂ decomposition, to produce H₂ and CO. We found that the stability of the membrane reactor was not more than 40 h, and the membrane significantly broke due to the erosion of the CO₂ and reducing

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atmospheres on the surface of the membrane. Therefore, besides the high stability in reducing atmosphere, the considerable CO₂-tolerated property is also important for the practical application of MIEC materials in catalytic membrane reactors. Carolan et al. [24] reported that A-site-deficient La_{0.2}Sr_{0.8}Co_{0.41}Fe_{0.41}Cu_{0.21}O_{3-δ} possessed a greater resistance against the corrosion of CO₂ than the A-site stoichiometric or A-site excess samples. However, few works about the development of the CO₂-tolerant MIEC materials were reported in literatures. In this work, we proposed a new kind of La_{0.85}Ce_{0.1}Ga_{0.3}Fe_{0.65}Al_{0.05}O_{3-δ} (LCGFA) MIEC oxide with good stability in both CO₂ and H₂ atmospheres. Meantime, the crystal structure, thermal expansion behavior, mechanical strength and oxygen permeability of this oxide were also investigated. The main purpose of this work is to develop a sort of potential MIEC material with sufficient thermal and chemical stability, high mechanical strength, and applicable oxygen permeability for catalytic membrane reactor.

2. Experimental

2.1. Sample synthesis

LCGFA powders were synthesized by the conventional solid-state reaction method. Stoichiometric amounts of analytical grade La₂O₃, CeO₂, Ga₂O₃, Fe₂O₃ and Al₂O₃ were mixed and ball-milled in ethanol for 24 h. The resulting slurry was fully dried at 100 °C and then calcined at 950 °C for 10 h. The as-prepared LCGFA powders were grinded, sieved (300 meshes) and then uniaxially pressed at 400 MPa to prepare the green disc membranes with the diameter of 16 mm. The LCGFA membrane was obtained after the green disc was sintered at 1250 °C for 10 h. The sintered membranes were polished to 1.0 mm in thickness before being used in the oxygen permeation measurements. The densities of the sintered membranes were determined by the Archimedes method, and the densities exceeded 90% of the theoretical value. For the comparison of membrane performance, a dense asymmetric LCGFA membrane (with a thin dense membrane layer and a porous support layer) was also prepared via a dry pressing technique and co-sintering route. LCGFA oxide together with about 20 wt.% active carbon, which acted as the porous former, were used for the preparation of porous support layer. The thickness of membrane layer was controlled by the amount of the added materials. The detail procedure about the preparation of the asymmetric membrane can be found in our previous work [25]. In addition, a mixed conducting oxide Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) was also prepared for the comparison of material properties.

2.2. Characterization

The crystal structures of the samples were characterized by X-ray diffraction (XRD, D8-advance, Bruker, Germany) using Cu Kα radiation. The experimental diffraction patterns were collected at room temperature by step scanning in the range 20° ≤ 2θ ≤ 80° with an increment of 0.05°. The thermal expansion behaviors of the samples were investigated by a dilatometry (Netzsch, DIL 402C, Germany) in air, nitrogen and carbon dioxide atmospheres (at a flow rate of 30 ml(STP) min⁻¹) with a heating rate of 5 °C min⁻¹ to 1000 °C. The sintering behaviors of the samples were also investigated by the dilatometry in still air with a heating rate of 2 °C min⁻¹ to 1250 °C. All the samples had the dimensions of 6 mm × 6 mm × 20 mm. The three-point bending strengths of the samples were measured by a material testing machine (MTS, CMT6203, USA). The bending strength was calculated from the fol-

lowing equation:

$$\sigma = \frac{1.5FL}{bh^2} \quad (1)$$

where σ is the bending strength, in MPa; F is the fracture load, in N; L , b and h are the span length, width and height of the sample, respectively, in m. The cross-heading speed is 0.5 mm min⁻¹. For each composite, five samples were tested to get an average strength. The morphologies of the membranes were examined by scanning electron microscopy (SEM) (FEI, Model Quanta-2000, Holland). The working parameters of the SEM are as follows: high voltage (HV) 25–30 kV, work distance (WD) 8–10 mm and Spot 3.0.

2.3. Oxygen permeation measurement

Oxygen permeation measurements were carried out in a vertical high-temperature gas permeation system reported in our previous work [2,3]. Disk membrane was sealed between two gold rings and the edge of the disk was surrounded with ceramic sealant. The effective area of the membrane for oxygen permeation was about 0.283 cm². Before starting the oxygen permeation measurement, the assembly was heated from room temperature to 1040 °C at 2 °C min⁻¹ and held for 4 h to ensure the softening of the gold rings. Gas leakage, if present, could be detected by monitoring the nitrogen concentration in the effluent from the permeate side. The inlet gas flow rates were controlled by mass flow controllers (Models D07/ZM, Beijing Jianzhong Machine Factory, China), which were calibrated by a bubble flowmeter. Both sides of the membrane were maintained at atmospheric pressure. A programmable temperature controller (Model AI-708PA, Xiameng Yudian automation technology Co., Ltd.) was utilized to monitor the temperature around the membrane.

One side of the membrane was exposed to air at a flow rate of 120 ml(STP) min⁻¹, while the other side was exposed to a low oxygen partial pressure that was controlled by regulating the He flow rate at the range of 20–80 ml(STP) min⁻¹ using mass flow controller. The oxygen partial pressure gradient across the membrane was kept at about 2.1 × 10⁴/3 × 10² Pa. In addition, the oxygen permeation fluxes of the membrane under air/He + 20% CO₂ and air/He + 5% H₂ gradients were also tested. The flow rates of the gas (He + CO₂ or He + H₂) in permeation side were kept at 30 ml(STP) min⁻¹. The effluent streams were analyzed by on-line gas chromatographs (Shimadzu Model GC-8A, Japan). An internal standard gas CH₄ (about 1.0 ml(STP) min⁻¹) was added to the effluent streams and passed through the on-line analysis loop. The chromatograph was operated under a current of 180 mA and the attenuation of 1, conditions under which a trace amount of oxygen (>1 Pa) could be detected.

3. Results and discussion

3.1. Crystal structure and stability analysis

Fig. 1 shows the XRD patterns of the LCGFA powder and LCGFA membrane. LCGFA powder was multiphase and mainly composed of perovskite phase and CeO₂ phase. The XRD pattern of LCGFA sample was similar to that of (La, Sr)(Ga, Fe)O_{3-δ} oxides [26]. After sintered at 1250 °C for 10 h, LCGFA membrane was still composed of two phases; however, the intensity of characteristic peak of CeO₂ phase greatly decreased. The content of CeO₂ phase was roughly estimated according to the XRD data. They were about 7.38% and 4.76% in LCGFA powder and disk, respectively. This result indicates that CeO₂ phase is hard to dissolve into the perovskite main phase and the solid solubility increased with increasing the temperature and prolonging the time.

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