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A dense oxygen separation membrane with a layered morphologic structure

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Abstract

A configuration of dense mixed ionic and electronic conducting (MIEC) membrane with layered morphological structure for oxygen separation, which combines the benefits of high oxygen permeation flux of cobalt-based membrane, high chemical stability of iron-based perovskite and high mechanical strength of thick membrane, was studied. The membrane is normally composed of two layers; each layer is a dense MIEC oxide. The substrate layer is a thick dense membrane with high oxygen permeability but relatively lower chemical stability. The feasibility of dense thick $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF5582) membrane as the substrate layer and $Ba_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (BSCF5528) as the thin-film layer was mainly experimentally investigated. Both the BSCF5582 and the BSCF5528 show the same cubic perovskite structure and the similar lattice constant with no detrimental reaction products formed. By optimizing fabrication parameters of a simple dry pressing process, dual-layered membrane, free of cracks, was successfully fabricated. The oxygen permeation flux of a dual-layered membrane with the thin-film BSCF5528 layer facing to the sweep gas reached 2.1 mL cm^{-2} min^{-1} [STP] (1.56×10^{-6} mol cm^{-2} s^{-1}) at 900 °C, which is about 3.5 times higher than that of the BSCF5528 membrane (0.6 mL cm^{-2} min^{-1}, [STP] (4.46×10^{-7} mol cm^{-2} s^{-1}) under the same conditions.

Keywords: Perovskite; Oxygen permeation; Asymmetric membrane; Mixed conductor; Layered structure

1. Introduction

A large class of composite oxides possesses mixed ionic and electronic conductivity at elevated temperatures [1–3]. Dense ceramic membranes made of such materials allow oxygen to permeate through under the drive of oxygen partial pressure gradient across the membrane. The main potential applications of such membranes include oxygen separation from air and as membrane reactor for selective oxidation of hydrocarbon to value-added products [4–10].

For practical application, mixed ionic and electronic conducting (MIEC) membranes should possess sufficient high oxygen permeation flux and enough high operational stability to compete with the currently available oxygen generation techniques [11,12], such as distillation of cryogenic air. However, a dilemma was usually observed for the membranes based on single-phase conducting oxide, i.e., the higher the oxygen permeability the lower the chemical stability [13,14]. For the membranes with high chemical/structural stability such as iron-based perovskite, in order to obtain the oxygen permeation fluxes with practical attractiveness, surface modification, thin-film and dual-phase configurations are proposed [15–28]. The surface modification with a porous layer of oxide possessing high oxygen surface exchange kinetics was extensively studied recently [15–18]. Although significant improvement in permeation flux was sometimes observed, the absolute flux was still too low for practical application purpose due to the low oxygen bulk diffusion rate and the thick membrane configuration [18]. On the other hand, porous substrate supported thin-film oxygen separation membranes have been investigated by several researchers [19–23]. In order to avoid the solid-state reaction between the support and the thin-film layer, the application of the same material both for the porous substrate and the thin-film layer was proposed [23]. However, one technical difficulty about such configuration is how to densify the thin film while maintain the support, composed of the same material, in a highly porous state. Fur-

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thermore, one possible drawback of the thin-film membranes is their reduced mechanical strength. The dual-phase membranes have also been widely investigated which allow the oxygen ion and electron transport through the separated phases, borrowed the concept from the composite cathode in solid oxide fuel cells [24–28]. Unfortunately, such membranes usually show low oxygen permeability due to the non-ideal mixing of the two phases [25–28].

In order to improve the stability of high oxygen permeable membrane such as $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ (LSCF), Wachsman et al. first introduced the concept of dual-layer membrane with a thin protecting layer of samaria doped ceria (SDC) on the low P_{O_2} side of main $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ (LSCF) membrane [29]. By adopting the similar concept, here, we report a configuration of dense MIEC membrane with layered morphological structure for oxygen separation, which combines the benefits of high oxygen permeation flux of cobalt-based membrane, high chemical stability of iron-based perovskite and high mechanical strength of thick membrane. The membrane is composed of two or more layers; each layer is a dense MIEC oxide. The main layer, or called as the support or substrate layer, is a thick dense membrane with high oxygen permeability but relatively low chemical stability, which is composed of oxide such as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF5582). The other layer(s) is in thin-film configuration, which has the similar composition to the support layer but with a higher chemical and structural stability and relatively lower oxygen permeability, such as $Ba_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (BSCF5528). The oxygen permeation flux of this new layered membrane was found to be about one order of magnitude of higher than that reported by Wachsman et al., further the problem of phase reaction between SDC and LSCF layers was avoided in this study.

2. Experimental

2.1. Synthesis of powder

All the composite oxide powders investigated in this study were synthesized by a sol–gel or auto-combustion process based on an EDTA-citrate complexing method. The detailed preparation procedure for the EDTA-citrate complexing sol–gel process can refer to our previous publication [30]. For the auto-combustion process, NH_4NO_3 was introduced to the normal EDTA-citrate process as the combustion aid. The preparation of 0.1 mol of BSCF5582, for example, is schematically described in Fig. 1. The 0.05 mol $Ba(NO_3)_2$, 0.05 mol $Sr(NO_3)_2$, 0.08 mol $Co(NO_3)_2$ and 0.02 mol $Fe(NO_3)_3$ (all in analytic grade) were dissolved in de-ionized water within a 1 L Pyrex beaker under magnetic stirring. 58.45 g EDTA acid, dissolved in 150 mL NH_4OH (28 wt.%), was dropped to the mixed solution. Precipitation might occur after the addition of EDTA. 84.06 g citric acid was added under stirring and heating until a clear solution was obtained, followed by the addition of 100 g NH_4NO_3 as combustion aid. The solution was constantly heated at 90 °C under stirring to form a gel, which was then transferred to a pre-heated oven at 250 °C for a self-propagated combustion. A highly loose packed powder was obtained from the auto-combustion, which was then calcined at 500–1000 °C for 3–5 h for later application.

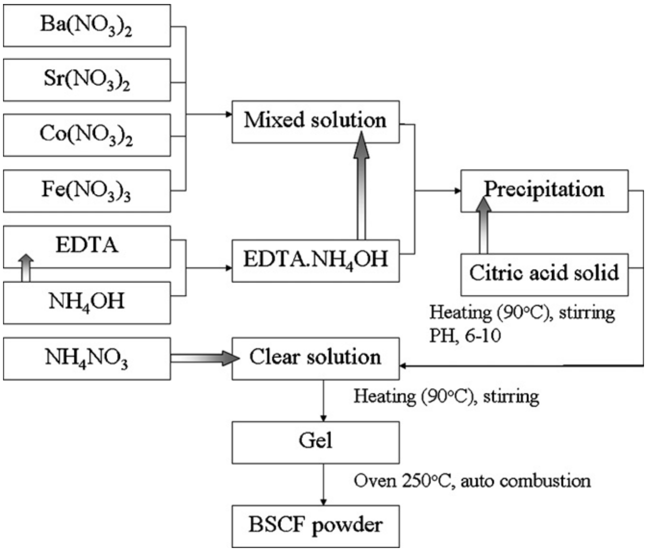

Fig. 1. Schematic diagram for the preparation of BSCF powder via the NH_4NO_3-assisted auto-combustion process.

2.2. Asymmetric membrane fabrication

Dry pressing technique, which has been frequently applied it in the preparation of thin-film electrolyte solid oxide fuel cells [31–34], was used for the fabrication of asymmetric dense membranes with layered morphologic structure in this study. The preparation of a dual-layer oxygen separation membrane, for example, is schematically shown in Fig. 2. Weighed amount of substrate powder was dry pressed using a 15 mm stainless steel die under a hydrolytic load of 2.8 tonnes. After holding under the load for several minutes, the pressure was released and the top part of the die (Part A) was removed to expose one surface of the substrate disk to ambient air. The exposed substrate surface and inner wall of the die were cleaned by a high-flow air stream to get rid of the loosely attached particle. Calculated amount of oxide powder for the thin-film layer was then added onto the substrate surface. The top part of the die (Part A) was re-positioned and turned gently to make the powder distributed over the substrate surface homogeneously in thickness. A higher load of ~4.2 tonnes hydrolytic force was then applied for several minutes to form the green dual-layered membrane. After release from the die, the green membranes were sintered to dense pellets under the controlled atmosphere (air, oxygen or nitrogen) at a temperature of 1000–1100 °C for 2–10 h with the heating/cooling rate of 1–5 $°C\,min^{-1}$.

2.3. Characterization

The crystal structure of the synthesized powders was characterized by X-ray diffraction (XRD, Bruker D8 Advance) using Cu Kα1 radiation. The lattice constants of the powders were calculated by UnitCell. The morphological and compositional features of the prepared membranes were examined