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A dense oxygen separation membrane deriving from nanosized mixed conducting oxide

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Abstract

In this paper, nanosized $SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$ (SCFZ) powders, which were synthesized via a flame aerosol synthesis (FAS) method, were successfully used to fabricate oxygen separation membranes with densified structure. XRD, TEM (HRTEM), O_2-TPD and TG were used to characterize the crystal structure, morphology, oxygen desorption property and oxygen non-stoichiometry of SCFZ-FAS powders. The densification process and the oxygen permeability of the SCFZ-FAS membranes were examined by SEM and the high temperature oxygen permeation measurements. The as-produced SCFZ-FAS powders were of the typical perovskite structure with high degree of crystallinity. Hard agglomerations, which were induced from the high temperature of the flame, were found among the nanosized rod-like SCFZ-FAS particles. Compared with SCFZ synthesized by the traditional solid-state reaction (SSR) method, the densification temperature of SCFZ membranes was reduced and the oxygen permeation flux was increased by 40% at the elevated temperatures (1073–1223 K) when SCFZ-FAS powders were used as the starting material. Long-term oxygen permeation measurement (1123 K, 180 h) showed that SCFZ-FAS possessed stable structure under low oxygen partial pressure (about 10^{-3} atm) environment.

Keywords: Nanosized material; Mixed conducting oxide; Flame aerosol synthesis method; Oxygen permeation

1. Introduction

Owing to the great potential applications in oxygen separations, solid oxide fuel cells (SOFC) and membrane reactors [1–6], mixed ionic-electronic conducting (MIEC) oxides have stimulated extensive interests in developing new materials and optimizing known materials in recent years [7–9]. The main advantages of the dense ceramic membranes made of MIEC materials are related to a theoretically absolute permselectivity to the oxygen, which is based on the special oxygen transport mechanism of MIEC oxides [1]. For example, technologies for the partial oxidation of methane (POM) to syngas, which are based on the MIEC exhibiting both high oxygen ionic and electronic conductivities at elevated temperatures [1,10,11], can thereby combine the oxygen separation and the partial oxidation process in one membrane reactor. This eliminates a costly oxygen separation plant that is used in the traditional POM units [12].

Teraoka et al. [13] were the first to report very high oxygen fluxes through cobalt-rich $La_{1-x}Sr_xCo_yFe_{1-y}O_{3-\delta}$ perovskite-type oxides, which were about 2–4 orders of the magnitude higher than those of the stabilized zirconia at the same temperatures. Since then, increasing attentions have been attracted on the study of the compositions [7,8,14,15], the synthesis processes [16–20] and various kinds of the MIEC membranes (tubular, hollow fiber and asymmetric membranes) [3,21–31], in which some researches aimed to figure out the correlations between the composition, synthesis process and the microstructure, properties (the electric conductivity, oxygen permeability and structure stability) of the MIEC oxides. For the practically commercial uses, an oxygen flux of about 1–10 ml cm^{-2} min^{-1} (7.4×10^{-7}–7.4×10^{-6} mol cm^{-2} s^{-1} (STP)) has been suggested as necessary [32,33]. However, the practical applications of the MIEC oxides are still hampered by some specific disadvantages of the materials, such as insufficient oxygen permeabilities and structure stabilities at high temperatures,

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especially the long-term phase stability in the reducing atmosphere [33,34].

Over the last decade, materials with nanostructures, such as nanoparticles, nanorods, nanowires, nanocubes and nanotubes, have drawn considerable attentions from the scientific and engineering researchers [35–38]. Stemming from the smaller size and the larger surface-to-volume ratio, nanostructured materials exhibit distinct properties from those of the bulk materials [38], and are considered as the promising candidates for realizing nanoscaled electronic, optical and mechanical devices [39]. For example, nanocrystalline YSZ exhibited superior mechanical, electrical and thermal properties as compared to its conventional coarse-grained counterparts [40–42]. The thriving nanotechnology provides a novel possible way to deal with the obstacles of MIEC oxides that mentioned above, and may be helpful to show deeper insight into the structural evolution from single atoms to crystalline solids. This is critically important not only in exploiting new membrane materials for the oxygen separation, but also in improving the performance of the existing dense ceramic membranes.

Many synthesis methods, such as the solid-state reaction (SSR) method, the modified citrate process and the citrate–EDTA complexing method, have been used in fabricating MIEC oxides [16,20]. One of the common grounds of these methods lies in an inevitable long-term calcination processes accompanied with grindings, which is necessary to fulfill the perovskite-type structure. This, not only increases the possibility of introducing the impurities, but also leads to the growth of grains and particles. More important, the long-term calcination processes aggravate the agglomeration of the particles, which significantly enhances the densification temperatures for the membranes. All these, besides spoiling the integrality and properties of the membranes, set an insurmountable barrier to fabricate nanosized MIEC oxides.

Flame aerosol technology, which refers to the formation of fine particles from gases in the flames, has been practiced since the prehistoric times [43]. Today, flame technology has been employed routinely in the large scaled manufacture of carbon blacks and ceramic commodities, such as the fumed silica and the pigmentary titania, and sometimes for the special chemicals as zinc oxides and alumina powders. In a general flame aerosol process, precursors are injected into a burner as gas, droplets, or even solid particles. Liquid or solid precursors rapidly evaporate and change into vapors as they are exposed to the high temperature flame. Vapors form intermediates, product molecules and clusters in the flame due to the high temperature, and quickly grow into nanosized particles because of the coagulations and/or surface reactions [44].

By applying the flame aerosol technology into the fabrication process of MIEC oxides, the long-term calcination and the grindings can thereby be avoided. Reactions among the precursor materials will complete in an instantaneous period of time in the high temperature flame, which ensures the formation of the perovskite-type oxides with nanostructures. The aim of this paper was thus to describe the fabrication process of the nanosized MIEC oxide via a flame aerosol synthesis (FAS) method. Characterizations were emphasized to compare the differences, such as the oxygen permeability of the dense MIEC membranes, between the nanosized MIEC oxide/membrane and their bulk counterparts. The perovskite-type oxide of $SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$ (SCFZ), which had been studied in our lab [45], was chosen in this work because of its high oxygen permeation flux and stable crystal structure in the low oxygen partial pressure (about 10^{-3} atm).

2. Experimental section

2.1. Sample preparation

Fig. 1 presents the schematic diagram of the apparatus used for fabricating the nanosized SCFZ powders via a FAS method. Stoichiometric amounts of $Sr(NO_3)_2$, $Co(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and $Zr(NO_3)_4{\cdot}5H_2O$ (99.9%) were dissolved into a certain volume of the deionized water (the ratio between the deionized water and the metal nitrates was around 12) under continuous agitation, and used as the precursor materials (1).

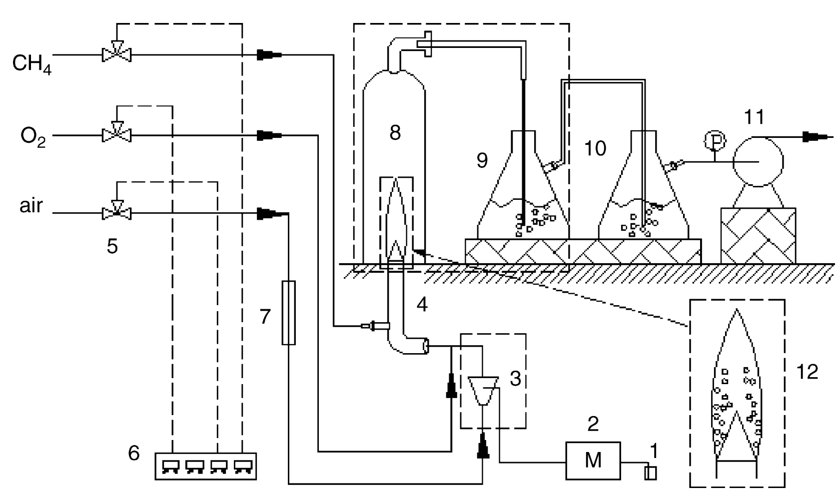

Fig. 1. Schematic diagram of the apparatus for synthesizing nanosized SCFZ by the flame aerosol synthesis method. (1) Precursor solution; (2) liquid feed pump; (3) atomizer; (4) burner; (5) flow control valve; (6) flow controller; (7) desiccator; (8) bell glass; (9) gas washing bottle; (10) tail gas absorber; (11) vacuum pump; (12) flame.