

A dense oxygen separation membrane deriving from nanosized mixed conducting oxide

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Abstract

In this paper, nanosized $\text{SrCo}_{0.4}\text{Fe}_{0.5}\text{Zr}_{0.1}\text{O}_{3-\delta}$ (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.

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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 $\text{La}_{1-x}\text{Sr}_x\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ 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 $1\text{--}10\text{ ml cm}^{-2}\text{ min}^{-1}$ ($7.4 \times 10^{-7}\text{--}7.4 \times 10^{-6}\text{ mol cm}^{-2}\text{ s}^{-1}$ (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 $\text{SrCo}_{0.4}\text{Fe}_{0.5}\text{Zr}_{0.1}\text{O}_{3-\delta}$ (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 $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (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).

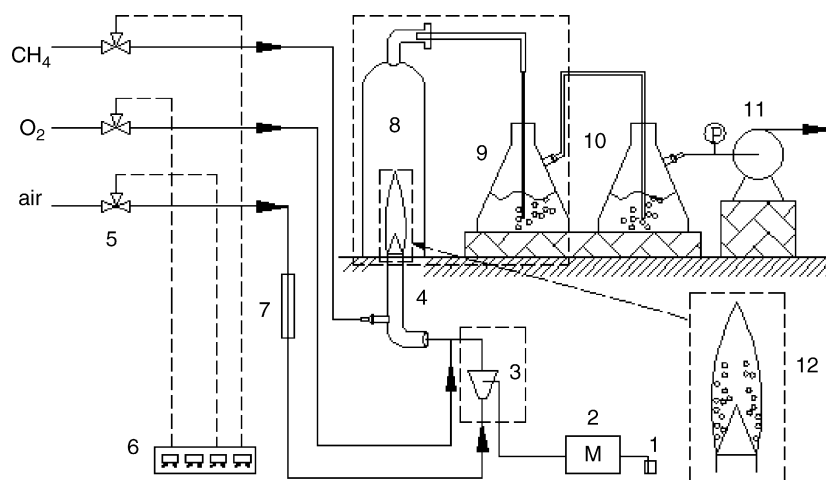


Fig. 1. Schematic diagram of the apparatus for synthesizing nanosized SCFZ by the flame aerosol synthesis method. (1) Precursor solution; (2) liquid feed pump; (3) atomizer; (4) burner; (5) flow control valve; (6) flow controller; (7) desiccator; (8) bell glass; (9) gas washing bottle; (10) tail gas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

Precursors were quantitatively sent to an atomizer (3) by a liquid feed pump (2) (BT-01-100, Baoding Longer Precision Pump Co. Ltd., China). Fully dried air ($6.01\text{--}9.01\text{ l min}^{-1}$ (STP)), together with the precursors, passed through the atomizer and the precursor materials changed into small droplets before meeting methane (99.999% , $0.6\text{--}0.9351\text{ l min}^{-1}$ (STP)) at the feed port of the burner (4). The flows of the gases, such as the air and methane, were controlled by the mass flow controllers (6) (model D07/ZM, Beijing Jianzhong Machine Factory, China). The burner, which was made of a quartz tube (12 mm i.d.), was made long enough to ensure the intensive mixing of the fuel (methane), the air and the droplets of the precursors. SCFZ-FAS particles, the production rate of which can be adjusted from about $1\text{--}10\text{ g h}^{-1}$, formed in the flame (12) (about 10 cm of the height) and were collected by the isopropyl alcohol (9). Tail gas (CO_2) was purged into the sodium hydroxide solution (10) and was then directly vented into the atmosphere by a vacuum pump (11). SCFZ-FAS powders were gained by evaporating the isopropyl alcohol at about 308 K. The as-gained powders were dried and uniaxially pressed at about 1000 MPa to prepare the green disc membranes with the diameter of about 16 mm. The corresponding membranes were obtained after the green discs were sintered at 1173, 1273 and 1373 K, respectively, for 2 h in static air with a heating and cooling rate of 1 K min^{-1} .

For comparison, the solid-state reaction (SSR) method was used to prepare SCFZ powders at the same time, which was described elsewhere [45]. The SCFZ-SSR powders were grinded, sieved (300 meshes) and then uniaxially pressed at 400 MPa to prepare the green disc membranes with the diameter of about 16 mm. Corresponding membranes were obtained after the green discs were sintered at 1473 K for 5 h in static air with a heating and cooling rate of 2 K min^{-1} .

2.2. Characterizations

Crystal structures of SCFZ-FAS and SCFZ-SSR were determined by the X-ray diffraction (XRD, Bruker D8 Advance) using $\text{Cu K}\alpha$ radiation. The experimental diffraction patterns were collected at room temperature by a step-scanning mode in the range of $20^\circ \leq \theta \leq 80^\circ$ with the increment of 0.02° s^{-1} . Morphologies of the nanoscaled SCFZ-FAS particles were observed by the transmission electron microscopy (TEM) and high-resolution TEM (JEM-2010 UHR, Japan). All the samples were directly taken from the apparatus (Fig. 1) in the synthesis process to ensure the observation of the original state of the materials fabricated. The oxygen non-stoichiometry of SCFZ-FAS in N_2 was determined using the thermogravimetric analysis (TG). TG was carried out with a NETZSCH STA 409 PC system in the temperature range of 313–1223 K with a heating rate of 10 K min^{-1} . O_2 -temperature programmed desorption (O_2 -TPD) analysis was performed on the chemisorptions equipment (CHEMBET-3000, Quantachrome Instruments). Samples were loaded in a quartz glass tube. After the pretreatment in O_2 at 1073 K for 1 h, the temperature was slowly decreased to 373 K in the same atmosphere. Then the oxygen desorption experiment was conducted by increasing the temperature to 1273 K at a rate of 10 K min^{-1} in pure helium, and the oxygen desorbed was

monitored by a thermal conductivity detector. Scanning electron microscopy (SEM, QUANTA-2000) was used to observe the microstructures of the SCFZ-FAS membranes sintered at different temperatures.

The oxygen permeation measurement was performed on a high temperature oxygen permeation apparatus in our laboratory, which was described elsewhere [46]. Disk membranes were polished to the same thickness of about 0.8 mm and sealed between two gold rings. The effective area for the oxygen permeation was about 0.283 cm^2 . Before starting the oxygen permeation measurement, the assembly was heated from room temperature to 1313 K at a rate of 2 K min^{-1} and held for 4 h to form the bonding between the membrane and gold rings. Temperature of interest was then adjusted by controlling the cooling rate (2 K min^{-1}). The feed side of the membrane was exposed to air ($P_{\text{O}_2} = 0.209\text{ atm}$) at a flow rate of 100 ml min^{-1} , while the permeate side of the membrane was exposed to a lower P'_{O_2} that was controlled by regulating the He (99.999%) flow rate by mass flow controllers (model D07/ZM, Beijing Jianzhong Machine Factory, China). A gas chromatograph (GC, Shimadzu model GC-8A) equipped with a 5A molecule sieve column was connected to the outlet of the oxygen permeator. The amount of oxygen permeating through the membrane was calculated by measuring the outlet flow rates and the oxygen content.

3. Results and discussions

3.1. Crystal structure analysis

Fig. 2 shows the XRD patterns of SCFZ-FAS and SCFZ-SSR powders, in which the perovskite phases of SCFZ-SSR and SCFZ-FAS were of the cubic perovskite structure (Table 1) with the similar crystal cell volume and the interplanar spacing (d_{110}). Besides this, small amount of SrZrO_3 was detected in both of the two samples in Fig. 2. The formation of the SrZrO_3 phase in SCFZ-SSR was considered to be the result of a solid-state reaction between ZrO_2 and the perovskite phase ($\text{SrCo}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$) in the long-term calcination process (1223 K, 5 h) [45]. For SCFZ-FAS, the appearance of the SrZrO_3

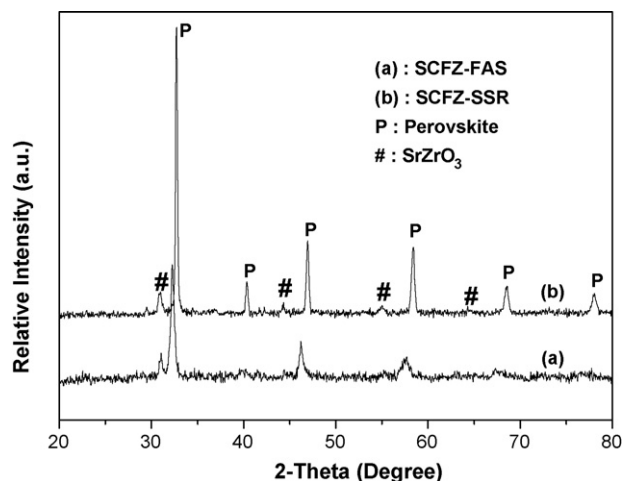


Fig. 2. XRD patterns of (a) SCFZ-FAS and (b) SCFZ-SSR powders.

Table 1
Lattice parameters of SCFZ-SSR and SCFZ-FAS

Sample	Lattice parameters (Å) ($a=b=c$)	Cell volume (Å ³)	Crystal system	$P(1\ 1\ 0)$ (2-theta) ^o	d_{110} (Å)
SCFZ-SSR	3.89(1)	58.91	Cubic	32.767	2.73
SCFZ-FAS	3.88(6)	58.68	Cubic	32.452	2.76

phase could be considered as an indication that complete reactions among the precursor materials were shortened to in an instantaneous period of time (between 1 and 10^{-5} s [47]) in the high temperature flame (which was reported to be about 2000 K [48]) by the FAS method. The diffraction peaks of the perovskite phase of SCFZ-FAS were found to be of slightly lower diffraction angles, lower intensities and broader widths than those of SCFZ-SSR. This might be derived from: (1) the size-related features of the small size (nanosized) particles, which has been widely discussed for the single crystal nanoparticles [35] and (2) a slight variation of the composition of the perovskite phase of SCFZ-FAS, which is due to the different sizes of the starting materials when synthesizing the SCFZ oxides [45].

3.2. Morphology of the SCFZ-FAS particles

Typical TEM images of the nanoscaled SCFZ-FAS particles were shown in Fig. 3(a). SCFZ-FAS were of the rod-like nanoparticles with the length-diameter ratio of about 8.6 (the inset in Fig. 3(a)). Several rod-like nanoparticles gathered together with the node at the center or the end of the particles. The agglomeration of the particles increased the secondary particle size of the material synthesized, which belonged to the microsize particles.

It is well known that, generally, two types of the agglomeration may exist when synthesizing the ceramic powders via a FAS method, which are the soft agglomerate and the hard agglomerate [49], respectively. The former can be taken apart by mechanical ball milling or ultrasonic disperse. For the hard agglomerate, particles combine intensively and form strong aggregates of high density. This can be somewhat taken apart at the expense of much higher energy. Owing to the fact that the as-prepared samples were directly taken from the gas washing bottle (9 in Fig. 1), in which the isopropyl alcohol was used to collect the powders and prevent the gathering of the particles, the formation of the agglomeration in Fig. 3(a) should be mainly due to the collision of the nanoparticles in the high temperature flame. Thus, this agglomeration belongs to the hard agglomeration. It should be noted that the formation of the hard agglomeration of the particles can be effectively prevented by optimizing the operation conditions and/or introducing electric field, which have been widely studied in the flame aerosol technology [44,50].

HR-TEM image of SCFZ-FAS particles were shown in Fig. 3(b), which clearly presented the polycrystalline perovskite structure with high crystallinity and the existence of sets of the structure defects. The arrangement of the atoms at the edge of the particle (white arrowhead in Fig. 3(b)) was much looser than that in the interior of the powder. The interplanar spacing

of d_{200} (1.96 Å) and d_{220} (1.39 Å) agreed well with the results from the XRD patterns (Fig. 2), which proved that the nanorods in Fig. 3(a) were SCFZ-FAS.

3.3. Non-stoichiometry and O₂ desorption properties

The oxygen non-stoichiometry of the SCFZ-FAS oxide in N₂ can be estimated from the TG data. Fig. 4 shows the TG curves of SCFZ-FAS and SCFZ-SSR powders recorded in N₂ atmosphere, in which the weight of SCFZ-FAS loses much faster than that of SCFZ-SSR. From the TG data, the oxygen non-stoichiometry

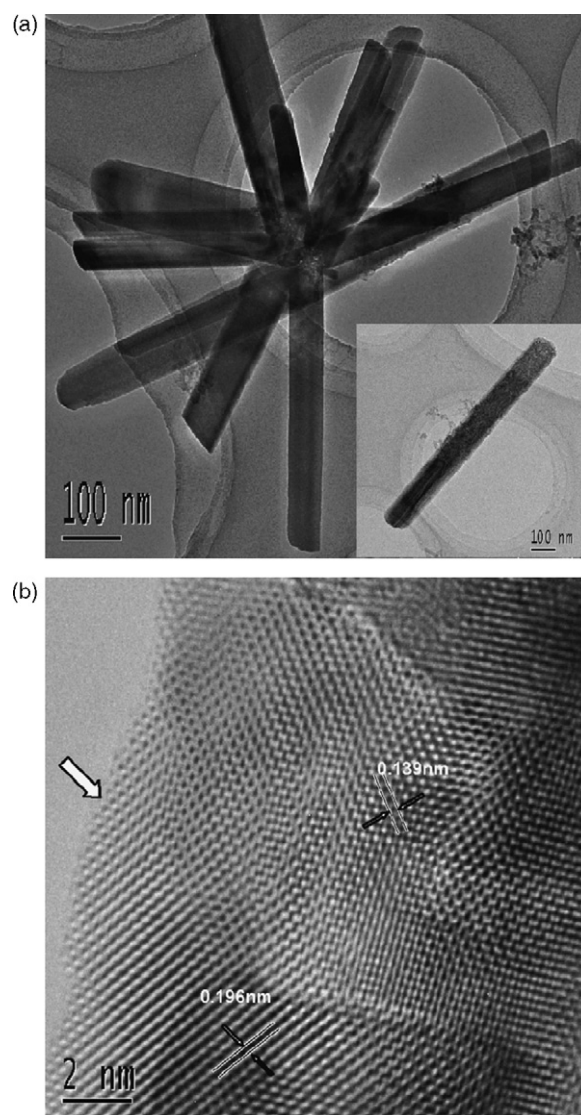


Fig. 3. (a) TEM images of the as-prepared SCFZ-FAS particles and (b) HRTEM image of the as-prepared SCFZ-FAS, interplanar spacing of 1.96 and 1.39 Å corresponded to the d_{200} and d_{220} of SCFZ, respectively.

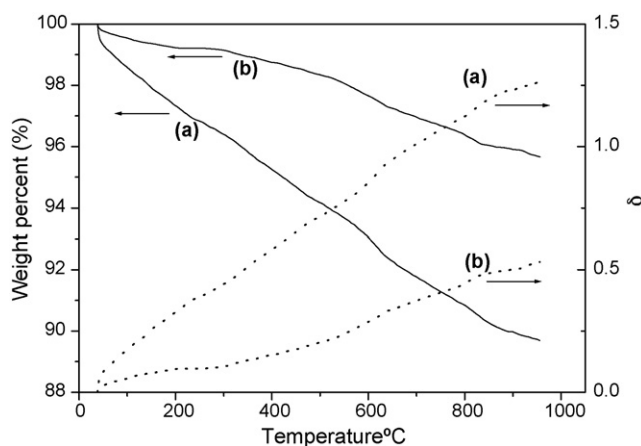


Fig. 4. TG (solid line) and oxygen non-stoichiometry (dot line) curves of (a) SCFZ-FAS and (b) SCFZ-SSR.

can be calculated using equation [51]:

$$\Delta\delta = \delta - \delta_0 = \frac{\Delta m}{m_0} \frac{M_{\text{mol}}}{M_0}$$

where M_{mol} is the molar weight of the complex oxide; M_0 the molar weight of oxygen; m_0 the weight of the sample under the initial conditions (T_0 and P_{O_2}) of experiment; $\Delta\delta$ and δ are the relative and absolute values of oxygen non-stoichiometry at all other values of T and P_{O_2} , respectively; δ_0 is the oxygen non-stoichiometry at the initial conditions. If we assume in this case that δ_0 is close to zero at room temperature [52], δ can be estimated roughly [19]. The estimated oxygen non-stoichiometry δ as a function of temperature in N_2 of SCFZ-FAS and SCFZ-SSR are also shown in Fig. 4. Compared with SCFZ-SSR, δ curves reveal that SCFZ made by the FAS method has a larger oxygen non-stoichiometry and the difference of δ between the two samples becomes more obvious at elevated temperature.

For the oxygen permeation process through a dense MIEC membrane, oxygen molecules are adsorbed on the feed-side surface of the membrane and dissociate into the oxygen anions. At the permeate-side surface, oxygen anions reassemble into oxygen molecules and are desorbed into the atmosphere of the lower oxygen partial pressure. This process is very similar to the temperature programmed desorption process of O_2 (O_2 -TPD). On the other hand, the desorption process of the oxygen in O_2 -TPD leads to the change of the valence state of the metal elements in the unit cell, which affects the configuration of the crystal cell, such as the BO_6 octahedron, and the stability of the perovskite structure. This is also analogous to the variations of the crystal structure of membrane materials in the oxygen permeation measurement. So, the analysis of the O_2 desorption properties of SCFZ-FAS cannot only be used to predict the oxygen permeability of MIEC, but also reflect the structural stability of the materials synthesized [45].

Generally, two desorption peaks will appear in an O_2 -TPD profile, which indicate two types of oxygen, α and β oxygen, respectively [53]. The peak below 900 K is always related to the desorption process of the oxygen (α oxygen) in the intrinsic oxygen vacancies of the materials, which were filled with oxygen in the pretreatment process. The peak above 1000 K associates with

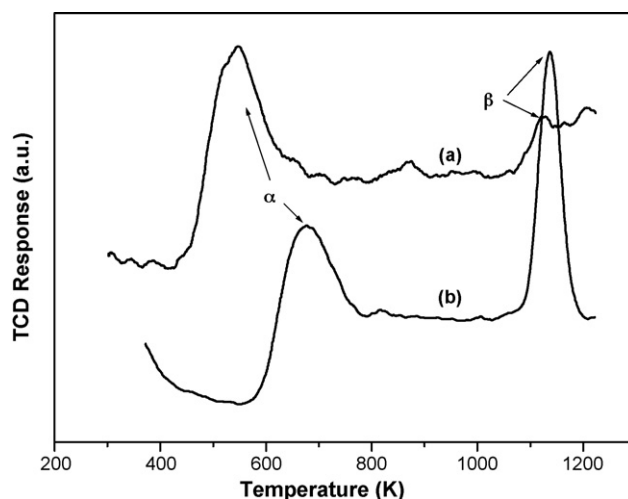


Fig. 5. O_2 -TPD profiles of (a) SCFZ-FAS and (b) SCFZ-SSR.

the desorption of the lattice oxygen (β oxygen), which derives from the reduction of Fe^{3+} or Co^{3+} to Fe^{2+} or Co^{2+} [53]. Fig. 5 shows the O_2 -TPD profiles of SCFZ-SSR and SCFZ-FAS. The peak area of the α oxygen of SCFZ-FAS was bigger than that of SCFZ-SSR, which indicated a larger content of the oxygen vacancies in SCFZ-FAS. Moreover, the peak corresponding to the α oxygen of SCFZ-FAS was about 150 K lower than that of SCFZ-SSR. This meant that, besides the larger surface to volume ratio, the nanostructure of SCFZ-FAS was also helpful for the oxygen to move from the interior part of the powder to the surface in the desorption process. All these agree well with the calculation results of the oxygen non-stoichiometry from the TG data (Fig. 4).

The peaks corresponding to the β oxygen of the two samples appeared almost at the same temperature, which was coincided with the mechanism of the formation of the β oxygen that mentioned above. Compared with SCFZ-SSR, much less β oxygen was observed in O_2 -TPD at about 1100 K, which might be an indication of the stable crystal structure of SCFZ-FAS at low oxygen partial pressure atmosphere.

3.4. Densification process of the SCFZ-FAS membrane

The green SCFZ-FAS disc membranes were sintered from 1173 to 1373 K for 2 h to examine the densification process of SCFZ-FAS, which is shown in Fig. 6(a)–(d). When the sintering temperature was 1173 K, little contraction occurred and the SCFZ-FAS membrane was porous. Large amount of the cavities (several microns in size) together with the gathering of the spherical particles (the particle sizes ranged from several hundred nanometers to about $2\text{ }\mu\text{m}$) were observed in the membrane, as shown in Fig. 6(a). Small gaps, instead of the cavities, formed and the shape of the particles turned from sphere to polyhedron when the sintering temperature was increased to 1273 K (Fig. 6(b)). Although obvious shrink of the membrane occurred, the membrane was still porous. The SCFZ-FAS membrane was finally densified when the sintering temperature reached 1373 K. The grains at the cross-section (Fig. 6(c))

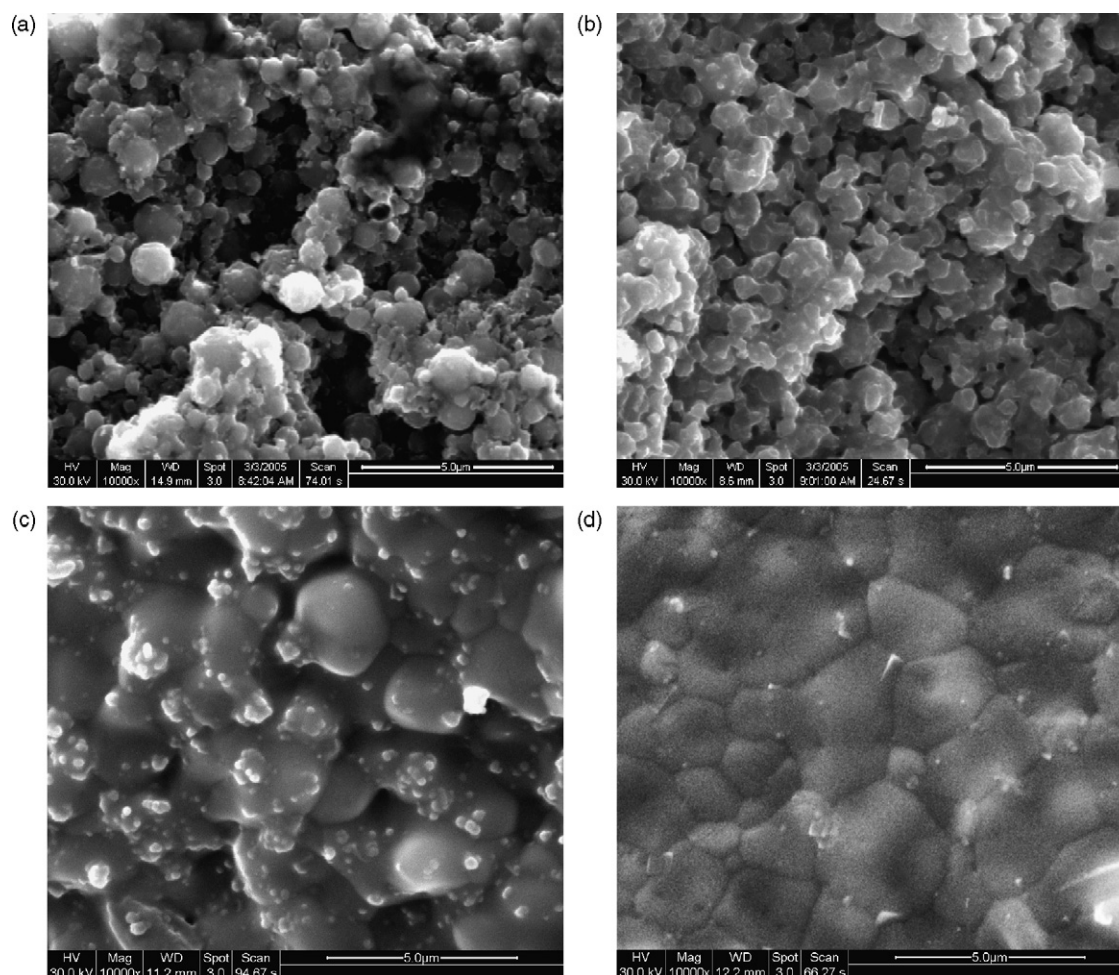


Fig. 6. SEM images of the cross-section of the SCFZ-FAS membranes sintered at (a) 1173 K, (b) 1273 K, (c) 1373 K and (d) the surface of SCFZ-FAS membranes sintered at 1373 K.

and the surface (Fig. 6(d)) of the membrane combined closely, and only very small amount of the airtight holes were found, which resulted from the diffusion of the grain boundaries. Owing to the smaller size and the larger surface-to-volume ratio of the nanoscaled materials, the densification temperature of the SCFZ-FAS membrane in our study was about 100 K lower than that of SCFZ-SSR. Similar results have been reported when nanoscaled ZrO_2 was used as the starting material in the preparation of the dense oxygen permeation membranes, in which a decrease of the densification temperature of about 100–200 K was achieved compared with the microcrystalline powders [54].

3.5. Oxygen permeability and stability of SCFZ-FAS membrane

The temperature dependence of the oxygen fluxes through the SCFZ-FAS and SCFZ-SSR membranes (0.8 mm in thickness) are shown in Fig. 7. SCFZ was derived from the perovskite-type oxide of $\text{SrCo}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$ (SCF) by partially substituting Fe with Zr [45]. In the previous report of our lab [55], introducing ZrO_2 decreased the content of oxygen vacancy and the variation of the oxygen non-stoichiometry of SCF, which suppressed the corresponding order–disorder phase transition and reduced

the apparent activation energy (E_a) for the oxygen permeation. In Fig. 7, single activation energy ($E_a = 47.1 \text{ kJ mol}^{-1}$) for the oxygen permeation was observed for the SCFZ-SSR membrane, which agreed well with the previous study [55].

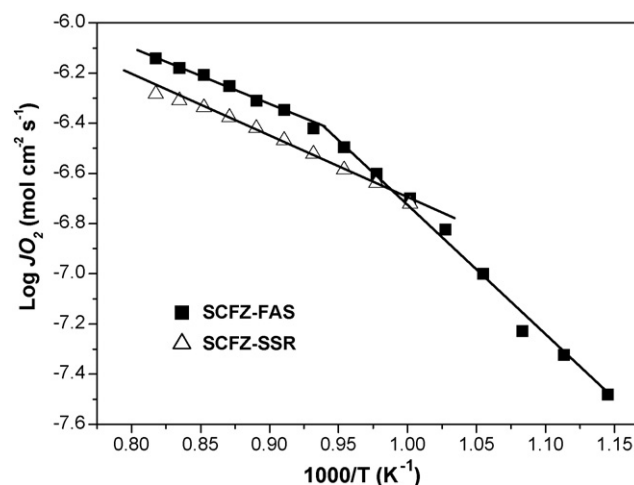


Fig. 7. Arrhenius plots of the temperature dependence of oxygen permeation fluxes through SCFZ-FAS (densified at 1373 K) and SCFZ-SSR membranes.

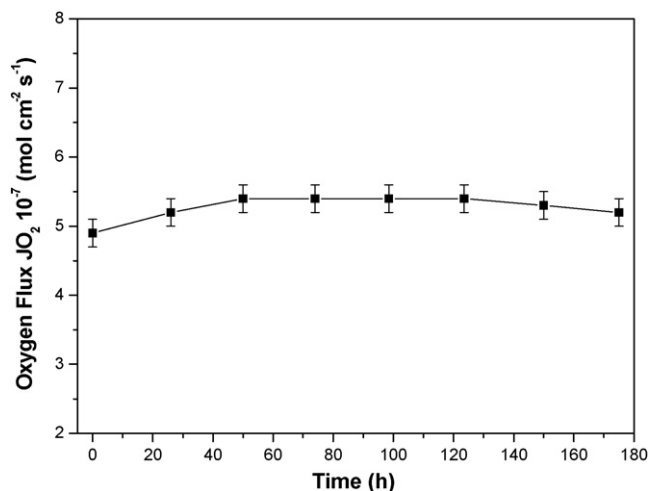


Fig. 8. Long-term oxygen permeation measurement of the SCFZ-FAS membrane (densified at 1373 K) at 1123 K for about 180 h.

Compared with the SCFZ-SSR membrane, the oxygen permeation flux of the SCFZ-FAS membrane was about 40% (about $0.4 \text{ ml cm}^{-2} \text{ min}^{-1}$) higher at the elevated temperatures (from 1073 to 1223 K) and E_a ($45.68 \text{ kJ mol}^{-1}$) was similar to that of SCFZ-SSR. This should be due to the formation of the more oxygen vacancies in SCFZ-FAS, which has been proved in the characterizations of TG (Fig. 4) and O_2 -TPD (Fig. 5). When the temperature was below 1073 K, the oxygen permeation flux became sensitive to the temperature and E_a rose to $104.49 \text{ kJ mol}^{-1}$. This indicated that the ordering of the oxygen vacancies occurred when the temperature was lower than 1073 K, which enhanced the resistance for the oxygen permeation (the increase of E_a) and weakened the mobility of the oxygen anions (the decrease of the oxygen permeation flux) [1,2,4,13,45,55].

After the investigation on the temperature dependence of the oxygen permeability, measurement of the time dependence of the oxygen flux on the same SCFZ-FAS membrane was continuously carried out at 1123 K for about 180 h (Fig. 8) to examine the stability of SCFZ-FAS at low oxygen partial pressure atmosphere (about 10^{-3} atm). When the oxygen permeation process reached the steady stage, the oxygen flux kept steadily at about $5.5 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$. No obvious change of the crystal structure was found on both the feed-side and permeate-side surfaces of the membrane (the related XRD patterns were not showed in this paper). This suggested that the crystal structure of SCFZ-FAS was stable at low oxygen partial atmosphere.

4. Conclusion

Nanosized $\text{SrCo}_{0.4}\text{Fe}_{0.5}\text{Zr}_{0.1}\text{O}_{3-\delta}$ (SCFZ) was fabricated by a flame aerosol synthesis (FAS) method in this paper. Compared with the traditional solid-state reaction (SSR) method, fabrication of the nanosized SCFZ was realized by avoiding the long-term calcinations with grindings, and SCFZ-FAS with high degree of crystallinity was fabricated in an instantaneous period of time in the flame. In contrast to SCFZ-SSR, SCFZ-FAS was of similar unit cell volume and interplanar spacing of d_{110} .

TEM images showed that the as-synthesized SCFZ-FAS particles were of the rod-like shape with hard agglomeration. The densification temperature of SCFZ-FAS membrane was 100 K lower than that of SCFZ-SSR membrane. Further steps can be applied to prevent the formation of the hard agglomeration in the high temperature flame and a lower densification temperature is expected. The oxygen permeation flux of SCFZ-FAS was about 40% (about $0.4 \text{ ml cm}^{-2} \text{ min}^{-1}$) higher than that of SCFZ-SSR at elevated temperatures (1073–1223 K), which was due to a larger non-stoichiometry in high temperature range. Long-term oxygen permeation measurement (1123 K, 180 h) showed that SCFZ-FAS was of stable structure under low oxygen partial pressure (about 10^{-3} atm). Our results also indicate that FAS can also be considered to fit for the fabrication of other MIEC oxides with nanostructures.

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