The effect of Strontium contents on novel MIEC1-MIEC2 dual-phase ceramic-based oxygen transport membranes

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Abstract. Although ceramic-based oxygen transport membranes (OTMs) have irreplaceable advantages over traditional oxygen production technologies, their oxygen permeability and stability need to be further improved. Based on the theoretical starting point of increasing the three-boundary reaction zone and reducing blocking effect, a set of new dual-phase membranes 75wt%Ce₀.₈Sm₀.₁Cu₀.₁O₂₋δ-25wt%-Sm₀.₈Sr₀.₂Co₀.₈Fe₀.₂O₃₋δ (CSC-8282) and 75wt%Ce₀.₈Sm₀.₁Cu₀.₁O₂₋δ-25wt%Sm₀.₃Sr₀.₇Co₀.₈Fe₀.₂O₃₋δ (CSC-3782) with different strontium contents were prepared by a one-pot sol-gel method ensuring that each element has the same chemical potential. The surface morphology, crystal structure and element distribution are systematically studied by SEM, XRD and EDS, which confirms that the synthesized membranes have an obvious dual-phase structure and excellent compactness. The results of the oxygen permeability experiment show that the oxygen permeability of CSC-3782 is always higher than that of CSC-8282 under any conditions due to the inducing effect of strontium on oxygen vacancies, and flow rate of CSC-3782 at 960°C reached 0.64 and 0.22mL·cm⁻²·min⁻¹ for He and CO₂ as a sweep gas, respectively. The final long-term stability test confirmed that the dual-phase composite membrane with great prospects for development has high temperature stability and CO₂-tolerant property, and the doping of strontium to A-site of perovskite contributes to the improvement of its performance.

1. Introduction

Inorganic dense ceramic-based OTMs have aroused widespread interests owing to their excellent potentials in new energy field and oxy-fuel process, such as membrane reactors for syngas production, pure oxygen separation and oxygen-enriched combustion for CO₂ capture. Although ceramic membranes show irreplaceable advantages over traditional oxygen generation technologies such as pressure swing adsorption (PSA), cryogenic distillation and polymeric membranes (comparisons of various oxygen generation technologies are shown in Table 1), two basic conditions must be met in order to achieve large-scale industrial applications: high oxygen permeability and corresponding excellent stability.
Table 1. The comparisons of oxygen production methods[1].

| Process          | Status   | Byproduct | Purity |
|------------------|----------|-----------|--------|
| Cryogenic        | Mature   | Excellent | > 99%  |
| PSA              | Semimature | Poor    | 95%    |
| Polymeric membrane | Semimature | Poor   | ~40%   |
| Ceramic membrane | Developing | Poor   | > 99%  |

In the past few decades, single-phase OTM materials have been widely studied in order to solve the above two conditions, such as BaFe$_{0.95-x}$Ca$_{0.05}$Ti$_x$O$_{3-δ}$, Pr$_{0.6}$Sr$_{0.4}$CuO$_{2-δ}$, La$_{0.6}$Ca$_{0.4}$Co$_{1-x}$Fe$_x$O$_{3-δ}$, BaFe$_{0.7}$Zr$_{0.2}$Y$_{0.1}$O$_{3-δ}$, SrFe$_{1.3}$Nb$_{0.3}$O$_{3-δ}$, SrCo$_{0.8}$Fe$_{0.2}$Mo$_{0.3}$O$_{3-δ}$[2-5]. In particular, Co-containing perovskite materials such as La$_{0.6}$Sr$_{0.4}$Co$_{1-x}$Fe$_x$O$_{3-δ}$[6], Ba$_{0.8}$Sr$_{0.2}$Fe$_{0.8}$O$_{2+δ}$[7] have shown excellent oxygen permeability. Unfortunately, the smaller binding energy of cobalt ion with oxygen promotes the rapid diffusion of oxygen and causes the extremely poor stability at the same time. In view of the problems faced by single-phase membranes, the researchers put forward the idea of dual-phase OTM materials, namely oxygen ions and electrons are transmitted in independent two-phase channels, thereby reducing the demanding requirements for a single material, Bi$_{1.5}$Y$_{0.3}$Sm$_{0.2}$O$_3$-Ag and Zr$_{0.6}$Y$_{0.4}$O$_{1.8}$La$_{0.7}$Sr$_{0.3}$MnO$_3$[8, 9] are the typical example. Although this kind of membranes has high stability, its permeation flux is far less than that needed in practical application. Subsequently, dual-phase OTMs composed of perovskite-type mixed ionic-electronic conducting (MIEC) materials and fluorite-type oxygen ionic conducting (IC) oxides have been extensively developed, such as Ce$_{0.9}$Pr$_{0.1}$O$_{2-δ}$-Pr$_{0.6}$Ca$_{0.4}$Fe$_{0.2}$O$_{3-δ}$, Ce$_{0.9}$Sm$_{0.1}$O$_{2-δ}$-SrCo$_{0.8}$Nb$_{0.2}$O$_{3-δ}$, Ce$_{0.9}$Gd$_{0.1}$O$_{2-δ}$-La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$, Ce$_{0.8}$Sm$_{0.2}$O$_{2-δ}$-Sm$_{0.6}$Sr$_{0.4}$Al$_{0.3}$Fe$_{0.7}$O$_{3-δ}$[10-12]. The strategic aim of (1) reducing the blocking effect of oxygen ions in bulk diffusion compared to IC-pure electronic conducting (EC) OTMs. The second point is (2) to increase the three-phase boundary (TPB) on the surface and oxygen surface-exchange reaction (OSER) of membranes, as shown in Figure 1 (b), (c).

In this work, considering the irreplaceable role of Co-containing perovskite materials with high flux in the study of membrane materials, MIEC1-MIEC2 dual-phase OTMs 75wt%Ce$_{0.8}$Sm$_{0.1}$Cu$_{0.1}$O$_{2-δ}$-25wt%Sm$_{0.8}$Sr$_{0.2}$Co$_{0.4}$Fe$_{0.2}$O$_{3-δ}$ (CSC-8282) and 75wt%Ce$_{0.8}$Sm$_{0.1}$Cu$_{0.1}$O$_{2-δ}$-25wt%Sm$_{0.8}$Sr$_{0.7}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (CSC-3782) with different strontium contents were prepared by one-pot sol-gel method for comparative analysis. In this process, the electronic conductivity of the ceria-based fluorite oxide with high oxygen ion conduction is improved by co-doping with Sm and Cu to form the MIEC materials. Its dual purposes are to reduce the blocking effect of electrons in the fluorite phase...
and further expand the TPB on the membrane surface to increase the active area, as shown in Figure 1 (d). In addition, the effect of strontium contents on this type of membrane has also been explored.

2. Experimental

2.1. Materials preparation

The preparation of precursor powder adopts sol-gel method, in short, the corresponding nitrates in a certain stoichiometric ratio was mixed and heated at 85°C with stirring, citric acid and EDTA with molar ratio of 1.5 times of total metal ions were also added to the solution and heated and stirred continuously. Heat the solution at 100°C for a long time until the solution becomes gelatinous after adjusting PH to 7-8 using ammonia solution. Subsequently, heated it with a flat plate furnace until it is black and fluffy and calcined at 850°C for 12h at a heating and cooling rate of 1°C/min in a muffle furnace under air atmosphere. Finally, the obtained powder ass pressed into compact block with a diameter of 15mm and a thickness of about 0.5mm using the tablet press (SPEX SamplePrep, America) at 150Mpa. Required circular membrane was prepared by sintering at 1250°C for 12h with a cooling and heating rate of 1°Cꞏmin⁻¹, and grinding and polishing.

2.2. Oxygen permeability measurement

The oxygen permeability is composed of a self-made ceramic tube and a stainless steel connection device[14]. The air on the feed side of the OTMs is synthesized by N₂ and O₂, the permeate side is swept by He and CO₂, and all the gas are controlled by the mass flow controllers (MFC, Seven star D07-19FM). The flow of outgoing gas is measured by soap bubble flowmeter, the concentration is monitored by the gas chromatograph (GC, Nanjing Kejie-GC5890, China) and the membranes are sealed by high-temperature ceramic sealant. The oxygen permeability $J_{O_2}$ is calculated by the following formula:

$$J_{O_2}(\text{mL}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}) = (C_{O_2} - C_{N_2})\times \frac{F}{S}$$

where $F$ is the flow rates of outgoing gas, $C_{O_2}$ and $C_{N_2}$ are the concentrations of O₂ and N₂, $S$ is working areas of membrane, and a ratio of the leaked nitrogen is 4.02 according to the theory of Kundsen diffusion.

2.3. Characterization

The material was characterized by X-ray diffraction (XRD, SmartLab, Cu Kα radiation). The $2\theta$ was in the range of 20-80° with an interval of 0.02°. The surface morphology analysis and energy dispersive X-ray spectroscopy (EDXS) analysis of the prepared material were measured on a scanning electron microscope (SEM, JSM-7800) at 15 kV acceleration voltage.

3. Results and discussion

3.1. Characterization of the material

The dual-phase membrane powder prepared by the one-pot sol-gel method in which each metal ion is mixed has obvious theoretical advantages compared with the solid-phase synthesis and the two-step method. Each element thus synthesized has the same chemical potential at each stage. Therefore, the diffusion of elements between fluoride and perovskite phases will be effectively averted during membrane operation. The XRD patterns of CSC-8282 and CSC-3782 dual-phase OTMs with different strontium contents obtained by dry pressing and sintering the powder are shown in Figure 2, and the 8282, 3782 and CSC single-phase oxides are also shown in the figure for comparative analysis. It can be seen that there are obvious two-phase diffraction peaks of perovskite and fluoride, and no other diffraction peaks due to adverse reactions, which indicates that the two phases coexist stably and have excellent compatibility. It also explains that the CSC-8282 and CSC-3782 composite oxides were successfully obtained by sol-gel and dry pressing methods. Compared with the pure perovskite and
fluorite phases, the diffraction peaks of the two dual-phase OTMs have slightly shifted, which means that the self-tuning of trace cations exists between the two phases. The phase composition of the two strontium content materials is similar, and the reflection intensity of the two phases can also reveal a 3 to 1 mass ratio.

![Fig. 2. The XRD patterns of the CSC, 8282, 3782 single-phase oxides and CSC-8282 and CSC-3782 dual-phase membranes heated at 1250°C.](image)

The SEM images of the sintered membrane surface are represented in Figure 3. It can be seen that the two separated crystal phases are both present in the two samples, which are extremely dense sintered at 1250°C. In addition, the mass ratio of the two phases was further confirmed, and the fluorite phase is much larger than the perovskite phase with an average grain size of 2um, which is related to the doping of Cu acts as a sintering aid and reduces the densification temperature, this has also been proven in other studies[15].

![Fig. 3. The SEM images of (a) CSC-8282 and (b) CSC-3782 dual-phase membranes.](image)

In order to explore the distribution of the two-phase elements and the phase formation in the bulk of studied membrane material, the EDS of CSC-3782 membrane and BSE for the cross-section have been completed. As shown in Figure 4, the diversity of average atomic numbers in two phases leads to the different colours representing fluorite and perovskite phases in the backscattering image. Therefore, it can be seen that in addition to the surface, the interior of the membrane is also extremely dense and has obvious phase distribution. The distribution of Ce and Sr representing fluorite and perovskite phases further reveals the self-tuning of trace cations, as shown in EDS analysis, a small amount of Ce enters into perovskite phase, and the trace of Sr is also observed in fluorite phase, which is similar to what Zhu et al.[16] found, we commonly still use nominal composition to define two different phase types.
3.2. Oxygen permeation performance

In order to explore the influence of strontium contents on the performance of this series of MIEC1-MIEC2 dual-phase membranes, we used a self-made device to test the relationship between the oxygen permeability of the two membranes and the temperature. Figure 5 shows the oxygen permeability of membranes with different Sr contents in the temperature range of 800-960°C under Air/He conditions. Intuitive conclusion can be drawn that the oxygen permeability of all membranes increases with the raise of temperature, because high temperature provides more internal energy to overcome the potential barrier for the diffusion of oxygen ions[17].

On the other hand, the oxygen permeability of CSC-3782 is significantly higher than that of CSC-8282. Under the same conditions, when CSC-3782 reaches a flow rate of 0.64mL·cm⁻²·min⁻¹ at 960°C, while CSC-8282 can only achieve a flow rate of 0.49mL·cm⁻²·min⁻¹. The best explanation for this phenomenon is that the raise in the doping amount of strontium to the A-site of perovskite leads to an increase in the oxygen vacancies generated in the perovskite phase lattice.
Fig. 6. Arrhenius plots of CSC-3782 and CSC-8282 under He sweep conditions.

Figure 6 shows the Arrhenius plots for CSC-3782 and CSC-8282 under Air/He conditions. It can be seen that the apparent activation energy of CSC-3782 and CSC-8282 in the temperature range of 800-960°C are calculated as 84.2 and 90.6kJ/mol, respectively, and their values are negatively correlated with oxygen permeability. The smaller activation energy and the larger pre-exponential factor of CSC-3782 indicate that the energy required for the diffusion of oxygen ions to break through the potential barrier is lower and the number of active sites are larger, which is also the reason for high oxygen permeability.

Fig. 7. The reversibility of the oxygen permeability through CSC-3782 and CSC-8282 as a function of time at 960°C under He and CO₂ sweeping conditions. Air flow rate: air flow rate: 150mlꞏmin⁻¹, He/CO₂ flow rate: 50mlꞏmin⁻¹.

Figure 7 shows the reversibility of the oxygen permeability through CSC-3782 and CSC-8282 as a function of time at 960°C under He and CO₂ sweeping conditions. When the sweep gas is switched from He to CO₂, the oxygen permeability of CSC-3782 and CSC-8282 decreases to 0.22 and 0.18mL·cm⁻²·min⁻¹, which is due to the adsorption of CO₂. While the sweep gas is converted to CO₂ again, the oxygen permeation flow of CSC-3782 and CSC-8282 can instantly return to the initial values of 0.64 and 0.49mL·cm⁻²·min⁻¹. Compared with the single-phase membrane, which even reaches the oxygen flow rate of 0mL·cm⁻²·min⁻¹ under the condition of CO₂ sweeping and cannot restore the initial value, the prepared dual-phase membranes have relatively excellent stability. In addition, regardless of the purging conditions, the oxygen permeability of CSC-3782 is always higher.
than that of CSC-8282, which also shows that strontium doping can promote the permeation flux of this type of dual-phase membrane.

![Graph showing permeation flux over time](image)

**Fig. 8.** Long-term test of CSC-3782 OTMs at 960°C. Air flow rate: 150 ml·min⁻¹, CO₂ flow rate: 50 ml·min⁻¹.

An excellent oxygen permeable membrane not only has a high oxygen permeability, but also needs to have good CO₂ stable reduction-tolerant. In order to verify the stability of CSC-3782 dual-phase, the relationship of its oxygen permeability with time was tested at 960°C, and the results are shown in Figure 8. It can be seen that the oxygen flow fluctuates around 0.22 mL·cm⁻²·min⁻¹ with long-term operation, which proves CSC-3782 excellent stability.

### 4. Conclusions

New type of MIEC₁-MIEC₂ dual-phase OTMs 75wt%Ce₀.₈Sm₀.₁Cu₀.₁O₂−δ–25wt%Sm₀.₈Sr₀.₂Co₀.₈Fe₀.₂O₃−δ and 75wt%Ce₀.₈Sm₀.₁Cu₀.₁O₂−δ–25wt%Sm₀.₃Sr₀.₇Co₀.₈Fe₀.₂O₃−δ with different strontium contents were successfully prepared by the one-pot sol-gel method. XRD results show that perovskite and fluorite coexist stably and have excellent compatibility. SEM and EDS show that the two phases of the composite material are distributed obviously according to the mass ratio and extremely dense. Cu doping also reduces the densification temperature of the membrane. Oxygen permeability experiments show that the oxygen permeability of CSC-3782, which has a lower apparent activation energy, is higher than that of CSC-8282, whether He or CO₂ is used as a sweep gas. The oxygen permeability of both membranes increases with rising temperature, and flow rate of CSC-3782 at 960°C reached 0.64 and 0.22 mL·cm⁻²·min⁻¹ for He and CO₂ as a sweep gas, respectively. The final stability test shows that the strontium-containing composite material has good high temperature resistance and stability under CO₂ conditions, so it has great potential in industrial applications based on OTMs.

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