Tantalum stabilized SrCoO$_{3-\delta}$ perovskite membrane for oxygen separation

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**Abstract**

The mixed ion and electron conducting oxides of SrCo$_{1-y}$Ta$_y$O$_{3-\delta}$ ($0 \leq y \leq 0.3$) powders were prepared by solid state reaction. By doping 10 mol% of tantalum on the B-site of SrCoO$_3$, the cubic perovskite structure of the SrCoO$_3$ is stable and a high oxygen permeation flux is achieved. The phase structure of the perovskite-type oxide of SrCo$_{0.9}$Ta$_{0.1}$O$_{3-\delta}$ was characterized by X-ray diffraction (XRD) and oxygen temperature-programmed desorption (O$_2$-TPD) revealing that SrCo$_{0.9}$Ta$_{0.1}$O$_{3-\delta}$ exhibits a good phase structure stability and reversibility in air. The oxygen permeation is predominated by oxygen ion bulk diffusion at the temperature $\geq 900$ C. During the long-term operation, the SrCo$_{0.9}$Ta$_{0.1}$O$_{3-\delta}$ membrane is operated at 900 C for more than 520 h with a steady oxygen permeation flux of around $1.36 \times 10^{-6}$ mol/s cm$^2$ with a membrane thickness of 0.65 mm under He/air gradient.© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Oxygen is ranked among the top five in the production of commodity chemicals in the world [1]. Commercial oxygen is currently produced by cryogenic distillation and pressure swing adsorption (PSA) and both are energy-consuming technologies. Recently, it was found that the perovskite with mixed oxygen ionic and electronic conductivities can be used for the oxygen separation from air at high temperatures [2]. Because of its infinite selectivity for oxygen, mixed oxygen ionic and electronic conducting (MIEC) membranes have a potential application in air separation. However, an industrial scale application based on such MIEC membranes has still not been realized. For practical applications, a MIEC membrane must (1) have a considerably high oxygen permeation flux under the operation conditions; (2) be stable for a long-term operation; (3) have enough mechanical strength for constructing the membrane module; (4) be cheap. It was reported that SrCo$_{0.9}$Ta$_{0.1}$O$_{3-\delta}$ (SCF) [2] exhibited a high oxygen permeation flux of $2.3 \times 10^{-6}$ mol/s cm$^2$ under an air/He oxygen gradient at 850 C. Because of the high oxygen permeation flux of SCF, its properties such as the conductivities, oxygen permeability, surface exchange kinetics and the stability were widely investigated [3–7]. Unfortunately, it was found that the SCF exhibits a poor chemical and structural stability at low oxygen partial pressure atmospheres [5–7]. Shao et al. developed a novel Ba$_{0.5}$Sr$_{0.5}$Co$_{0.9}$Fe$_{0.2}$O$_{3-\delta}$ (BSCF) using Ba to partially substitute Sr and found that the BSCF exhibits high oxygen permeation and good stability for the oxygen separation and the POM reaction [8,9]. ZrO$_2$ or YSZ doped SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ have also been proven to have a high oxygen permeation flux, stable structure and high mechanical strength [10], although a potential problem of the mismatch of the thermal expansion coefficient between the two phases is not solved. To further improve the stability of the membrane materials, cations with constant valance (Zr$^{4+}$, Ga$^{3+}$, Al$^{3+}$) [11–15] were used to partially substitute the reducible B-site ions (Co$^{3+}$, Fe$^{3+}$). Liu et al. [16,17] developed a novel perovskite-type mixed-conducting membrane based on SrCo$_{0.95}$Co$_{0.05}$O$_{3-\delta}$ with good oxygen permeability. Shao et al. reported that SrCo$_{0.9}$Nb$_{0.1}$O$_{3-\delta}$ exhibits a high electronic conductivity and oxygen permeability [18]. Additionally, a relatively steady permeation flux for more than 200 days under an air/helium oxygen gradient was reported for SrCo$_{0.9}$Nb$_{0.1}$O$_{3-\delta}$ membrane [19]. Very recently, our group developed a novel Ta stabilized BaCo$_{0.7}$Fe$_{0.2}$Ta$_{0.1}$O$_{3-\delta}$ (BCFT) for oxygen permeation and POM [20,21]. It was found that BCFT exhibits good oxygen permeation (around $1.18 \times 10^{-6}$ mol/s cm$^2$ at 950 C with a membrane thickness of 1.0 mm) and an excellent stability (more than 420 h long-term operation for POM).

In the present work, tantalum was used to partially dope on the B-site of SrCoO$_{3-\delta}$. Because it is located on the same group as niobium and the diagonal position of zirconium, tantalum should possess similar properties to niobium and zirconium. It can be expected that tantalum doped SrCoO$_{3-\delta}$ should possess compromise properties of zirconium doped SrCoO$_{3-\delta}$ [10] and niobium doped SrCoO$_{3-\delta}$ [19], i.e. higher oxygen permeation flux and more excellent stability. Therefore, the oxides of SrCo$_{1-y}$Ta$_{y}$O$_{3-\delta}$ ($0 \leq y \leq 0.3$) were prepared and the structure stability as well as the oxygen permeation was investigated in detail.

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2. Experimental

$\text{SrCo}_{1−x}\text{Ta}_x\text{O}_3$ ($y = 0.0, 0.01, 0.05, 0.1, 0.2, 0.3$) oxide powders were synthesized by a simple solid state reaction with $\text{SrCO}_3$, $\text{Co}_2\text{O}_3$ and $\text{Ta}_2\text{O}_5$ (all in analytical grades) as the raw materials. The as-synthesized powders were isostatically pressed into disk membranes under a pressure of 18 MPa in a stainless steel module with an inner diameter of 16 mm. Then the membranes were sintered at 1100°C for 10 h. Densities of sintered membranes were determined by the Archimedes method using ethanol. Only those membranes that had relative densities higher than 95% were chosen for oxygen permeation studies. The gas-tightness of the sintered membranes should be tested at room temperature before they were used for the oxygen permeation experiments.

The phase structure was characterized using a Bruker D8 Advance diffractometer (XRD) with Cu Kα radiation. The diffraction data were collected with a step scanning mode. Oxygen temperature-programmed desorption ($\text{O}_2$-TPD) was performed on Micromeritics AutoChem II 2920™. The purity of all gases ($\text{O}_2$, $\text{H}_2$, $\text{He}$, $\text{Ar}$) used in $\text{O}_2$-TPD and permeation studies was 99.999%.

Before oxygen desorption, the sample (about 1.0 g) was pre-treated in flowing oxygen at a flow rate of 30 ml/min at 900°C for 2 h and was cooled down to 40°C with a cooling rate of 10°C/min. Then $\text{O}_2$-TPD was performed from 40 to 950°C with a heating rate of 10°C/min and He was used as the carrier gas. The amount of desorbed oxygen was detected by a thermal conductivity detector (TCD). In order to investigate the reversibility of oxygen adsorption and desorption, the sample after $\text{O}_2$-TPD was pre-treated again in flowing oxygen at 950°C, and then the next $\text{O}_2$-TPD run was performed.

Oxygen permeation experiments were performed in a homemade high temperature permeator which can be found in our previous paper [22]. Both surfaces of membranes were polished with 1000 mesh SiC sand paper. A gold paste was used to seal the membrane onto a dense corundum tube. The sidewall of the membrane was also covered with the Au paste to avoid the radial release of oxygen. After assembling the permeation cell, the temperature was increased to 950°C with a heating rate of 2°C/min and held at 950°C for 3–5 h to seal the membrane on the corundum tube. An effective area surface of the membrane after sealing was 0.785 cm².

Dry air was fed on the air side and helium was fed on the sweep side of the membrane. Flow rates of the gases were controlled by mass flow controllers. A gas chromatograph (Shimadzu GC-14B) equipped with a TDX-01 column for the separation of oxygen and nitrogen was connected to the exit of the sweep side. The GC was frequently calibrated using standard gases mixtures of oxygen in helium in order to ensure a high reliability of the experimental data. The oxygen leakage is less than 2%, which was subtracted when the oxygen permeation flux was calculated. The calculation of oxygen permeation flux was presented elsewhere [23].

3. Results and discussion

Fig. 1 shows the XRD patterns of $\text{SrCo}_{1−y}\text{Ta}_y\text{O}_{3−δ}$ oxides with $0 ≤ y ≤ 0.3$. All of the oxides were prepared by the same preparation procedure. In Fig. 1, both $\text{SrCo}_{0.9}\text{Ta}_{0.1}\text{O}_{3−δ}$ and $\text{SrCo}_{0.95}\text{Ta}_{0.05}\text{O}_{3−δ}$ are a distorted BaNiO$_3$-type hexagonal phase. When the Ta content increases to 10%, i.e. $\text{SrCo}_{0.9}\text{Ta}_{0.1}\text{O}_{3−δ}$, a cubic perovskite structure is observed. With a further increase of Ta content to 0.2 or higher, some impurity diffraction peaks appear which are indexed to the phase of $\text{Ta}_2\text{O}_5$. It indicated that the small amount of Ta (5–10 mol%) doping on the B-site of $\text{SrCoO}_3$−δ can effectively make the cubic perovskite phase stable.

Fig. 2 presents the profiles of the $\text{O}_2$-TPD for $\text{SrCo}_{1−y}\text{Ta}_y\text{O}_{3−δ}$ ($y = 0.0, 0.01, 0.05, 0.1$). There are two oxygen desorption peaks ($\alpha$-peak and $\beta$-peak). The $\alpha$-peak at the low temperature zone (250–500°C) is corresponded to the reduction of Co$^{3+}$ to Co$^{2+}$. The $\beta$-peak at the high temperature zone (>700°C) is attributed to the reduction of Co$^{3+}$ to Co$^{2+}$ [20,22,24], which leads to a larger expansion of the lattice because of a big difference in the ionic radii between Co$^{3+}$ (63 pm) and Co$^{2+}$ (74 pm). With the increase of Ta doping, the peak area of $\alpha$-peak increases while the peak area of $\beta$-peak gradually decreases. The result revealed that the introduction of Ta$^{5+}$ can restrain the reduction of Co$^{3+}$ to Co$^{2+}$ and avoid a large change of the lattice, which can improve the stability of $\text{SrCoO}_3$.

In order to investigate the phase reversibility of $\text{SrCo}_{0.9}\text{Ta}_{0.1}\text{O}_{3−δ}$, the multi-run $\text{O}_2$-TPD was performed, as shown in Fig. 3. From the multi-run $\text{O}_2$-TPD profiles, it can be seen that four-run $\text{O}_2$-TPD profiles are the same which indicates that $\text{SrCo}_{0.9}\text{Ta}_{0.1}\text{O}_{3−δ}$ possesses good phase reversibility during the repetition of oxygen adsorption and desorption. After multi-run $\text{O}_2$-TPD, the sample was characterized by XRD, as shown in Fig. 4. It is found that the perovskite structure is still kept implying that $\text{SrCo}_{0.9}\text{Ta}_{0.1}\text{O}_{3−δ}$ exhibits excellent structure reversibility.

Fig. 5 shows the oxygen permeation flux as a function of temperature under an air/He oxygen gradient with the membrane thicknesses of 0.65 mm and 1.36 mm. The oxygen permeation flux increases linearly with increasing temperature from 700 to 950°C. The average energies of activation for the oxygen permeation through the membranes with the thicknesses of 0.65 mm and 1.36 mm are 43 kJ/mol and 45 kJ/mol, respectively. An oxy-
permeation flux of 1.54 $\times 10^{-6}$ mol/s $\cdot$ cm$^2$ is obtained at 950 °C with a membrane thickness of 0.65 mm. It was reported that SrCo$_{0.9}$Fe$_{0.2}$O$_3$ \cite{2} exhibited a high oxygen permeation flux of $2.3 \times 10^{-6}$ mol/s $\cdot$ cm$^2$ under an air/He oxygen gradient at 850 °C which is higher than SrCo$_{0.9}$Ta$_{0.1}$O$_3$. Kruidhof and Qiu et al. \cite{5,7} reported that with the temperature decreasing oxygen vacancies states may transform from the disorder states to order states in some perovskite membranes, and these change would lead a sharp change of the oxygen permeation flux. However, in Fig. 5, the curves do not show such an acute change, which means that oxygen vacancies order/disorder transformation does not take place in the temperature range from 950 °C to 700 °C.

Fig. 6 presents the oxygen permeation flux as a function of He flow rate. The air flow rate is fixed at 150 mL/min. The oxygen permeation flux increases with increasing sweep He flow rate at a given temperature because the oxygen partial pressure decreases with increasing He flow rate and hence the driving force for the oxygen permeation is increased. However, the effect of He flow rate on the oxygen permeation flux became un-conspicuous at 800 °C because the oxygen partial pressure on the sweep side varies slightly with the change of He flow rate.

The oxygen permeation process through perovskite membrane consists of oxygen surface exchange and oxygen bulk diffusion. Either, or a combination of the two steps, may be the rate-determining step of the oxygen permeation. It is very important to clarify the rate-determining step of the oxygen permeation in order to optimize the operation conditions. If the oxygen permeation is controlled by oxygen bulk diffusion, reducing membrane thickness would be an effective way to increase the oxygen permeation flux; while if the oxygen permeation is rate-determined by oxygen surface exchange kinetics, the surface modification of the membrane is optimum to improve the surface exchange rate. Therefore, the rate-determining step of the oxygen permeation through SrCo$_{0.9}$Ta$_{0.1}$O$_3$ membrane was then investigated.

Fig. 7 shows the oxygen permeation flux as a function of oxygen partial pressure gradients. The oxygen partial pressure on the air side is kept constant at 0.21 atm, while the oxygen partial pressure on the sweep side is adjusted by changing He flow rate. The oxygen partial pressure on the sweep side is decreased by an increasing He flow rate. As a consequence, the oxygen permeation flux increases because of the increase of the driving force for the oxygen permeation.

If the oxygen bulk diffusion is the limiting step for the oxygen permeation, according to Wagner theory the oxygen permeation flux through the membrane can be expressed as:

$$J_O = \frac{RT\sigma_e\sigma_i}{16F^2(\sigma_e + \sigma_i)L} \int P_0 \, d\ln(P_{O_2})$$

where $R$ is the gas constant; $F$ is the Faraday constant; $T$ is the temperature; $L$ is the thickness of the membrane; $P_0$ is the oxygen partial pressure on the air side; $P_i$ is the oxygen partial pressure on the He side, which depends on the oxygen permeation flux and He flow rate. $\sigma_e$ and $\sigma_i$ are the electronic and ionic conductivities, respectively. If the oxygen permeation flux through a perovskite-

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**Fig. 3.** Multi-run O$_2$-TPD profiles of SrCo$_{0.9}$Ta$_{0.1}$O$_3$ oxides.

**Fig. 4.** X-ray diffraction patterns of SrCo$_{0.9}$Ta$_{0.1}$O$_3$ before and after multi-run O$_2$-TPD.

**Fig. 5.** Dependences of the oxygen permeation flux through SrCo$_{0.9}$Ta$_{0.1}$O$_3$ membrane on temperatures.

**Fig. 6.** Effect of He flow rate on the oxygen permeation flux through SrCo$_{0.9}$Ta$_{0.1}$O$_3$ membrane. Membrane thickness = 0.65 mm.
Dependences of the oxygen permeation fluxes through SrCo0.9Ta0.1O3-
 membrane on ln(Pi/Po). Membrane thickness = 0.65 mm, temperature = 800–950 °C.

type membrane with electronic conductivity much higher than
ionic conductivity, and assuming that \( \sigma_i \) is constant, the formula
(1) can be integrated to

\[
J_{O_2} = \frac{RT \sigma_i}{16F^2L} \ln \left( \frac{P_h}{P_l} \right)
\]

When the membrane thickness \( L \) and the temperature are constant, the oxygen permeation flux \( J_{O_2} \) plotted against \( \ln(P_i/P_o) \) is linear and goes through the origin of the coordinates if the limiting step of the oxygen permeation is oxygen bulk diffusion. As shown in Fig. 7, the oxygen permeation flux increases approximately linearly with increasing oxygen partial pressure gradient \( \ln(P_i/P_o) \) at the temperature above 900 °C, which indicates that the oxygen permeation is mainly determined by bulk diffusion of oxygen ions. The oxygen permeation flux decreases slowly when the temperature is lower than 900 °C. At lower temperatures, the difference between the dash line and experimental data (shown in Fig. 7) becomes larger indicating that the rate-determining step has changed at the temperature < 900 °C. To further understand the rate-determining step during the oxygen permeation, the oxygen permeation fluxes through SrCo0.9Ta0.1O3-
 membrane with different membrane thicknesses are plotted as a function of the reciprocal of the thickness of membranes, as shown in Fig. 8. The dash lines in Fig. 8 show oxygen fluxes of the membranes if the transport of

the oxygen ions in the membrane bulk is the rate determining step. As shown in Fig. 8, when at the temperature ≥ 900 °C, the oxygen fluxes are mainly determined by the bulk diffusion of oxygen ions, which is in agreement with Fig. 7.

For the practical application, the long-term stability of the membrane is an important issue. Therefore, the long-term oxygen permeation operation of SrCo0.9Ta0.1O3-
 membrane was investigated at 900 °C. The oxygen permeation flux as a function of time is shown in Fig. 9. It can be seen that a steady oxygen permeation flux of around 1.36 × 10^{-6} mol/s cm^2 is achieved over the operation period of more than 520 h at 900 °C indicating that SrCo0.9Ta0.1O3-
 membrane exhibits a good stability for oxygen separation. The structures of fresh and spent membranes were characterized by XRD, as shown in Fig. 10. The membrane surfaces exposed to both air and He are mainly perovskite structure after the long-term permeation operation. However, there are some very small peaks for the membrane surface exposed to air which may be attributed to a Sr-enriched compound on the membrane surface exposed to air, as observed in the SEM-EDX (see Table 1).

The morphologies of fresh and spent membranes were observed by SEM, as shown in Fig. 11. The fresh membrane has clear grain boundaries, as shown in Fig. 11(a). The surface morphologies of the spent membrane after more than 520 h operation of oxygen permeation are different from the fresh membrane, as shown in Fig. 11(b)
and (c). From Fig. 11(b), no clear ceramic grains boundaries can be observed on the surface exposed to He side, which is different from the surface of the fresh membrane. However, EDX analysis shows that there is no big difference in the composition, as shown in Table 1. From Fig. 11(c) it can be seen that some particles deposit on the fresh membrane surface exposed to air, which imply that Sr is enriched on the membrane surface exposed to air after the long-term operation for oxygen separation. A similar phenomenon was reported in Ba0.5Sr0.5Co0.8Fe0.2O3−ı tubular membrane by Wang et al. [25]. After the removal of the surface particles by polishing using 2000 mesh sand paper, it can be seen that the membrane is still dense although the boundaries become blurry, as shown in Fig. 11(d).

4. Conclusion

The Ta doping concentration has a significant effect on the phase structure of the oxides SrCo1−yTa0yO4−δ (y = 0.0, 0.01, 0.05, 0.1, 0.2, 0.3). The proper Ta doping concentration in SrCo1−yTa0yO4−δ on the B-site to form a cubic perovskite is around 10 mol%. The multi-run O2−TPD profiles show that the SrCo0.9Ta0.1O3−ı exhibits excellent structure reversibility. The oxygen permeation through SrCo0.9Ta0.1O3−ı membrane is mainly determined by oxygen ion bulk diffusion at temperature ≥ 900 °C. The oxygen permeation flux of about 1.36 × 10−6 mol/s cm2 is achieved during more than 520 h permeation operation at 900 °C. XRD analysis shows that both sides of the spent membrane after more than 520 h oxygen permeation are similar to the fresh membrane in the phase structure, which indicated that the SrCo0.9Ta0.1O3−ı membrane exhibited a good structure stability and high oxygen permeation.

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References

[7] Z.P. Shao, W.S. Yang, Y. Cong, H. Dong, J.H. Tong, G.X. Xiong, Investigation of the permeation behavior and stability of Ba0.5Sr0.5Co0.8Fe0.2O3−ı oxygen membrane, J. Membr. Sci. 172 (2000) 177.


[21] Z.P. Shao, G.X. Xiong, Y. Cong, W.S. Yang, Synthesis and oxygen permeation study of novel perovskite-type BaBi$_x$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ ceramic membranes, J. Membr. Sci. 164 (2000) 167.

[22] H.H. Wang, C. Tablet, A. Feldhoff, J. Caro, Investigation of phase structure, sintering, and permeability of perovskite-type Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$, J. Membr. Sci. 262 (2005) 20.

[23] Z.P. Shao, G.X. Xiong, Y. Cong, W.S. Yang, Synthesis and oxygen permeation study of novel perovskite-type BaBi$_x$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ ceramic membranes, J. Membr. Sci. 164 (2000) 167.

[24] Z.P. Shao, G.X. Xiong, Y. Cong, W.S. Yang, Oxygen permeation study in a tubular BaBi$_x$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$, oxygen permeable membrane, J. Membr. Sci. 210 (2002) 259.