Oxygen-permeable ceramic membrane with improved medium-temperature stability based on partially A-site doped $K_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$

Pinhong Xie, Zhao Yijie, Yanmei Dong, Fang Li, Luyao Chen and Qiming Li

School of Petrochemical Engineering, Liaoning Petrochemical University, Fushun, Liaoning, P.R. China

**ABSTRACT**

Practical application of $SrCo_{0.8}Fe_{0.2}O_3$ (SCF) perovskite oxide for oxygen separation is hindered by poor stability. Here, we developed new $K_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane material by optimizing $K^+$ doping in A-site of prototypical SCF. The partial substitution of $Sr^{2+}$ with $K^+$ can lead to the enhanced mechanical strength and intermediate-temperature oxygen permeation stability. It is found that the doping content of $K^+$ should be lower than 20% because the excessive doping of $K^+$ in A-site of $SrCo_{0.8}Fe_{0.2}O_3$ can destroy their cubic perovskite structure. While $x \leq 0.2$, some diffraction peaks different from cubic perovskite can be evidenced by X-ray diffraction and their oxygen permeation flux also decreases rapidly. Among the fabricated membranes, $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}$ exhibits the highest oxygen permeation flux ($1.5 \text{ cm}^3 \text{ cm}^{-2} \text{ h}^{-1} \text{ atm}^{-1}$) at $950\text{°C}$ under an air/He gradient. More important is that $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}$ displays a stable oxygen permeation performance during over 120 h permeation operation at $750\text{°C}$.

1. Introduction

Dense mixed oxygen ionic and electronic conducting perovskite membranes exhibit a promising application in pure oxygen separation [1–3], partial oxidation of methane [4,5], cathodic materials of solid oxide fuel cells (SOFCs) [6,7], catalytic membrane reactors, etc. Especially, recent research has proven that the application of oxygen permeation membrane reactors might generate “greener processes” with lower consumption and higher selectivity because many selective oxidation reactions via permeated lattice oxygen ions can proceed more selectively than oxygen molecules derived from gas phase diffusion [8]. However, the industrial usage of oxygen permeation membrane modules mainly depends on two key factors such as high oxygen permeation flux and long-term oxygen permeation operation stability [9].

Teraoka et al. firstly developed $La_{1.0-x}Sr_xCo_{1.9}Fe_2O_{3-\delta}$ perovskite-based materials and found that $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ exhibits the highest oxygen permeation flux among $La_{1.0-x}Sr_xCo_{1.9}Fe_2O_{3-\delta}$ series [10]. Further research indicated that although $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ can meet the practical requirement of high oxygen permeation flux, its long-term oxygen permeation is hampered by poor chemical and structural stability [11], e.g. the cracking of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ membrane disks always occurs even at room temperature ambient. In addition, for $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, a phase transition from vacancy-disordered cubic perovskite to vacancy-ordered brownmillerite always occurs at approximately 800°C and concomitantly its oxygen flux can decay rapidly with the prolonged oxygen permeation time. To address this issue, the doping strategy in A-site or B-site of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ lattice is generally adopted to optimize their phase structure. Mostly alkaline earth metal elements or lanthanides such as Ba, Sr, or La were doped into A-site of perovskite oxides [12,13], and the B-site doped cations are generally transition metal elements such as Co, Fe, Zn, Cu, Cr, Al, etc. [14–16]. For instance, Zr cations are doped into $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ which obviously boosts their structural stability [17]. The doping of higher valent La$^{3+}$ in the lattice of SCFO can lead to an obvious increase in phase stability, but the oxygen permeability will decline due to the decrease of oxygen vacancies [18]. Nb cations were recently selected to synthesize $BaCo_{0.7}Fe_{0.3}NbO_3$ [19,20], which shows the outstanding oxygen permeation flux [19,20]. However, for most perovskite-based oxygen permeation membrane materials, there is a balance between the structural stability and oxygen permeation flux, i.e. the enhancement of the structural stability is always at the expense of their oxygen permeability [21]. For industrialized application, the oxygen permeation membrane modules should process both high oxygen permeation flux and high structural stability. Among them, the comparatively successful example is the development of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) through partially substituting $Sr$ by $Ba^{2+}$ [22,23]. Compared to SCFO, the tolerance factor of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ can be adjusted to around 1.0. Their lattice structure substantially takes advantages of the large radius and low valence of Ba$^{2+}$ to obtain a larger lattice cell volume and higher oxygen vacancy concentration. Hence, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}$...
K$_2$O$_{3.5}$ exhibits both the improved structural stability and optimal oxygen permeation flux. However, the gradual decay in oxygen permeation permeability below 800°C (intermediate-temperature range) is still unavoidable for Ba$_{0.2}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3.5}$ [24]. In short, the proper doping of metal ions in SCFO might optimize their phase stability or oxygen permeability, but there is still a great challenge in simultaneously improving both structural stability and oxygen flux. It is necessary to develop the new perovskite-based oxygen permeation materials with excellent intermediate-temperature stability and oxygen permeation flux.

To the best of our knowledge, the doping of the alkali metal ions is relatively unexplored due to their excessively low valence state and high bond energy. Recently, our group screened the doping of Na, K, Cs, and Li in A-site lattice of SCFO. Although the introduction of Li into SCFO can obtain pure cubic perovskite phase, the decomposition of Li-doped perovskite oxides easily occurs due to their high expansion coefficient. The pure cubic perovskite structure cannot be obtained by Na and Cs doping in SCFO due to their excessively large radius. Finally, we firstly developed K$_{1-x}$Sr$_x$Co$_{0.8}$Fe$_{0.2}$O$_{3-x}$ perovskite material for oxygen separation. By partial substitution of Sr$^{2+}$ with K$^+$ in SCFO, the mechanical and intermediate-temperature permeation stability of K$_{1-x}$Sr$_x$Co$_{0.8}$Fe$_{0.2}$O$_{3-x}$ can be greatly improved. It should be noted that the oxygen permeation flux of some optimized K$_{1-x}$Sr$_x$Co$_{0.8}$Fe$_{0.2}$O$_{3-x}$ sample is not decreased accompanying with the stability enhancement. In the present work, we mainly focus on the investigation of the intermediate-temperature stability and oxygen permeation flux of K$_{1-x}$Sr$_x$Co$_{0.8}$Fe$_{0.2}$O$_{3-x}$ series. The objectives of this work were also to discuss the effect of K$^+$ doping content on the structural stability and oxygen permeability of K$_{1-x}$Sr$_x$Co$_{0.8}$Fe$_{0.2}$O$_{3-x}$.

2. Experimental methods

The sample powders of K$_{5}$Sr$_{1-x}$Co$_{0.8}$Fe$_{0.2}$O$_{3-x}$ have been synthesized via a combined EDTA-citric acid complexing method [25]. KNO$_3$, Sr(NO$_3$)$_2$, Co(NO$_3$)$_2$, 6H$_2$O, and Fe(NO$_3$)$_3$·9H$_2$O with calculated stoichiometric ratio were mixed into the deionized water to form an aqueous solution. As complexing agents, EDTA acid and citric acid were then added into the above mixed solution with the final molar ratio of EDTA acid/citric acid/metal ions of 1:1:1.5. Subsequently, ammonia water was introduced into the solution until the pH value of the mixed solution was approximately 7.0. It can be found that a homogeneous purple solution can be obtained by continuous stirring. The obtained mixture was then heated to evaporate the water at 110°C until it was changed into a purple viscous gel. By further heating, the spontaneous combustion of the gel will take place and the precursor powders can be obtained. The resulting precursor powders were again sintered in a muffle furnace at 950°C for 300 min to get K$_{5}$Sr$_{1-x}$Co$_{0.8}$Fe$_{0.2}$O$_{3-x}$ oxide powders. K$_{5}$Sr$_{1-x}$Co$_{0.8}$Fe$_{0.2}$O$_{3-x}$ ceramic membrane disks were prepared by pressing to 30–40 MPa and sintering in a muffle furnace at 1200°C for 5 h. The dense K$_{5}$Sr$_{1-x}$Co$_{0.8}$Fe$_{0.2}$O$_{3-x}$ ceramic membrane disks were then formed for use after cooling to room temperature slowly.

The surface morphologies and elemental analysis of K$_{5}$Sr$_{1-x}$Co$_{0.8}$Fe$_{0.2}$O$_{3-x}$ membranes were characterized by a scanning electron microscope (SEM) (SU8010, Hitachi Co., Ltd, Japan) and metallographic microscope (XZJ-2030B, Fenghua Co., Ltd, China). The powder X-ray diffraction (XRD) measurement of K$_{5}$Sr$_{1-x}$Co$_{0.8}$Fe$_{0.2}$O$_{3-x}$ samples with different K$^+$ doping content was performed on a X-ray diffractometer (D8 Advance, Bruker Co., Ltd, German) equipped with Cu Ka radiation over the 2θ range of 10–70° (λ = 0.1540 nm).

Oxygen permeation test of K$_{5}$Sr$_{1-x}$Co$_{0.8}$Fe$_{0.2}$O$_{3-x}$ membranes was performed in our homemade apparatus, which was described elsewhere [26]. For oxygen permeation test, the membrane disks were firstly polished to certain thickness using 1000-mesh SiC papers. The membrane disk was then pasted onto the end of a quartz tube using a silver ring. The effective area for oxygen permeation was about 0.8 cm$^2$. For ceramic membrane sealing, the membrane disk should be slowly heated from room temperature to 963°C at a rate of 2°C min$^{-1}$ and held for 3.0 min to soften the silver ring. Then the operation temperature was quickly decreased to 950°C to solidify the molten silver ring. One side of the membrane was supplied with the synthesis air at a flow rate of 100 ml min$^{-1}$, and the permeated oxygen effluent through K$_{5}$Sr$_{1-x}$Co$_{0.8}$Fe$_{0.2}$O$_{3-x}$ membrane was swept by adjusting He flow rate. A gas chromatograph (GC, GC-3400) equipped with a 5 A molecule sieve column was connected to the exit of the permeate side. The oxygen permeation flux passing through the membrane was obtained based on the measured outlet flow rate and their oxygen concentration. Considering the error of tiny leaked N$_2$, the final oxygen permeation flux should be revised using the following equations:

\[
J_{O_2} \left( \text{ml} \cdot \text{cm}^{-2} \cdot \text{min}^{-1} \right) = \left( C_{O_2} - C_{N_2} \right) \frac{V_{O_2}}{V_{N_2}} \times \sqrt{\frac{M_{N_2}}{M_{O_2}}} \times F/A
\]

(1)

Herein, $J_{O_2}$ is the final oxygen permeation flux, and $C_{O_2}$ and $C_{N_2}$ are oxygen and nitrogen concentration in the outlet effluents detected by GC, respectively. $V_{O_2}$ and $V_{N_2}$ denote the volume percentage of O$_2$ and N$_2$ in the feed gas. $M_{O_2}$ and $M_{N_2}$ denote the molecular weight of...
O2 and N2. F is the measured outlet flow rate, and A is the permeation area of the ceramic membrane.

3. Results and discussion

3.1. XRD characterization

The room temperature XRD patterns recorded for the as-prepared K0.95Sr0.05Co0.8Fe0.2O3−δ oxides are presented in Figure 1. While the doping content of K+ in K0.95Sr0.05Co0.8Fe0.2O3−δ gradually increases from x = 0 to x = 0.5, these oxides are crystallized in approximate cubic perovskite structure. However, when the doping content of K+ was above x = 0.1, some extra diffraction peaks at 31.4°, 36.82°, and 42.78° can be observed, which cannot be indexed to cubic perovskite phase. Moreover, the diffraction intensity of these impure peaks gradually increases with the doping content of K+ (which can be seen from the dotted circles). It can be found that when the doping content of K+ is only x = 0.05 and x = 0.1, the pure cubic perovskite structure can be obtained. It should be noted that the equilibrium concentration of K+ in the SCFO perovskite oxides is slightly variable depending on their synthesis temperature. XRD analysis indicates that the doping capacity of K+ in A-site lattice of SCFO has a threshold value, which should be below x = 0.2. As we know that the radius of K+ in the 12 coordination is ca. 1.64 Å, which is much larger than that of Sr2+(1.44 Å), it is expected that the partial substitution of Sr2+ with K+ in SrCo0.8Fe0.2O3−δ lattice can induce the enlargement of the perovskite crystal cell volume [27], but it does not. As shown in Figure 1(B), the local magnified XRD diffraction peak ranging from 32° to 34° presents a complicated change in their unit cell volume. While x = 0.05, the characteristic peaks gradually shift toward to the lower diffraction angles, indicating the enlargement of perovskite unit cell. However, on continuously increasing the doping content of K+ from 0.1 to 0.5, the corresponding diffraction peaks again shift back to higher diffraction angles, which means that the perovskite unit cell volume tends to decrease again. The unexpected phenomenon should be further investigated in the future studies.

3.2. SEM-EDS characterization

The surface morphologies of K0.95Sr0.05Co0.8Fe0.2O3−δ, K0.95Sr0.05Co0.8Fe0.2O3−δ, and K0.95Sr0.05Co0.8Fe0.2O3−δ sintered at 1200°C are checked with SEM. As shown in Figure 2, it can be found that the doping of K+ in SCFO has a prominent impact on their surface microstructure. Figure 2(A) shows that the freshly prepared K0.95Sr0.05Co0.8Fe0.2O3−δ membrane without any polishing exhibits many clear grain boundaries and its grain size is mostly more than 10μm. The local magnified SEM image of K0.95Sr0.05Co0.8Fe0.2O3−δ is also given in Figure 2(B). It shows that the grains of K0.95Sr0.05Co0.8Fe0.2O3−δ exhibit the rippled appearance. When the doping content of K+ is increased to 0.1, K0.95Sr0.05Co0.8Fe0.2O3−δ displays completely different surface appearance, where the grain boundaries are difficult to be identified and the grains are tightly combined together (seen from Figure 2(C, D)). On further increasing the doping content of K+ such as x = 0.2, it can be found that the surface of K0.95Sr0.05Co0.8Fe0.2O3−δ tends to be more rough. Figure 2(E, F) shows that the surface indentations mainly exist in the grain boundaries on the membrane surface. In our experiment, three samples were sintered at the same temperature, but three samples exhibit totally different surface

Figure 1. X-ray diffraction data recorded for K0.95Sr0.05Co0.8Fe0.2O3−δ oxides that had been calcined at 950°C for 300 min (x = 0, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5).
Figure 2. SEM images of as-prepared K$_{0.05}$Sr$_{1-x}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ membranes. (A, B) K$_{0.05}$Sr$_{0.95}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$, (C, D) K$_{0.1}$Sr$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$, (E, F) K$_{0.2}$Sr$_{0.8}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$.

microstructure. It can be concluded that the introduction of K$^+$ changes not only the phase structure but also their surface morphologies. One possible explanation is that the doping content of K$^+$ can adjust their densification temperature of K$_{x}$Sr$_{1-x}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ and thus change their surface morphologies [28].

Figure 3 shows EDS elemental analysis of K$_{0.05}$Sr$_{0.95}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$, K$_{0.1}$Sr$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$, and K$_{0.2}$Sr$_{0.8}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ membranes. Here the grain boundary location is emphatically analyzed in order to analyze the distribution of potassium. As shown in Figure 3, the K$^+$ content of K$_{0.05}$Sr$_{0.95}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$, K$_{0.1}$Sr$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$, and K$_{0.2}$Sr$_{0.8}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ membranes are 0, 0.24, and 0.3 wt.%. Although SEM-EDS characterization can only give an approximate concentration of potassium, the EDS elemental analysis can reveal that the potassium element would aggregate to the grain boundary of K$_{x}$Sr$_{1-x}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$. Hence, the second phase different from cubic perovskite structure will be formed at the grain boundary if excessive K ions are introduced into SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ matrix, which is consistent with the above XRD analysis.

3.3. Effects of K$^+$ doping content on oxygen permeability

The oxygen permeation performance of K$_{x}$Sr$_{1-x}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ with different K$^+$ doping contents was investigated under air/He oxygen partial pressure gradient. As presented above, the surface morphologies of KSCFO are variable with different concentrations of K$^+$. In order to weaken the effect of the surface morphologies on oxygen permeation flux, all the membrane samples were polished with 1000-mesh sand papers. As shown in Figure 4, the oxygen permeability of all the samples gradually increases with improved temperature. It can be found that oxygen permeation flux of K$_{x}$Sr$_{1-x}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ ceramic membranes firstly increases and then decreases with the increase of K$^+$ doping content. For instance, K$_{0.05}$Sr$_{0.95}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ membrane exhibits the highest oxygen permeation flux whose oxygen flux at 950°C and 750°C were ca. 1.71 and 0.70 ml.min$^{-1}$.cm$^{-2}$, respectively. And the oxygen permeation flux of K$_{0.1}$Sr$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ membrane decreases to 1.58 ml.min$^{-1}$.cm$^{-2}$ at 950°C. Among them, K$_{0.2}$Sr$_{0.8}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ displays...
the lowest oxygen permeation flux of 1.38 ml.min⁻¹ cm⁻², which is even lower than that of SrCo₀.₈Fe₀.₂O₃₋δ. The oxygen permeation measurement indicates that a small amount of K⁺ doping in SCFO perovskite oxides...
Figure 4. Oxygen permeation flux of \( K_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta} \) with different \( K^+ \) doping content (membrane thickness = 1.5 mm).

helps to improve their oxygen permeation flux, but excessive doping of \( K^+ \) can degrade their oxygen permeation performance, which is in accordance with their XRD analysis. The effect of \( K^+ \) doping in perovskite oxides can produce complicated effects on their oxygen permeation flux. As we know that \( K^+ \) has a lower valence than \( Sr^{2+} \), and thus the doping of \( K^+ \) should improve the oxygen vacancy concentration in \( K_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta} \) oxide. However, excessive introduction of \( K^+ \) also results into the ordering of oxygen vacancies so that its oxygen flux should decrease [29]. In addition, the bond energy of \( K-O \) is higher than that of \( Sr-O \). Hence, excessive doping of \( K^+ \) has afforded a gradual degraded oxygen performance in our experiment. As a result, while \( x = 0.05 \) and 0.1, \( K_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta} \) perovskite materials process the pure cubic perovskite structure and superior oxygen permeation flux.

### 3.4. Structural stability and intermediate-temperature permeation stability of \( K_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta} \)

Besides oxygen permeation flux, the structural stability is another important factor to be considered in commercialization. Although \( SrCo_{0.8}Fe_{0.2}O_{3-\delta} \) was reported to have high oxygen permeation flux, the poor structural stability limits its practical application [30,31]. Figure 5 presents the optical photographs of \( K_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta} \) ceramic membranes kept in air at room temperature for 7 days. Although all the samples are sintered at the same temperature (1200°C), their structural stability is completely different. It can be found that the decomposition of \( SrCo_{0.8}Fe_{0.2}O_{3-\delta} \) membrane disk occurs due to higher expansion coefficient (Figure 5(A)). Nevertheless, both \( K_{0.05}Sr_{0.95}Co_{0.8}Fe_{0.2}O_{3-\delta} \) and \( K_{0.15}Sr_{0.85}Co_{0.8}Fe_{0.2}O_{3-\delta} \) maintain the intact membrane morphologies without any cracks as shown in Figure 5(B, C). The experimental results indicate that the doping of \( K^+ \) in \( SrCo_{0.8}Fe_{0.2}O_{3-\delta} \) can significantly improve their structural stability and inhibit the self-decomposition of membrane disks.

It was reported that severe oxygen permeation decay with time always take places for most perovskite-based materials below 800°C because of their poor thermodynamic stability. In our experiment, \( SrCo_{0.8}Fe_{0.2}O_{3-\delta} \) demonstrated a rapid decay in oxygen permeability in the 120-h oxygen permeation test at 750°C. It can be seen in Figure 6 that the initial oxygen permeation flux of \( SrCo_{0.8}Fe_{0.2}O_{3-\delta} \) membrane is about 0.64 ml.min\(^{-1}\).cm\(^{-2}\). After 80 h, its oxygen permeation flux dropped to be just 0.32 ml.min\(^{-1}\).cm\(^{-2}\). Compared to \( SrCo_{0.8}Fe_{0.2}O_{3-\delta} \)
O$_{3-\delta}$, K$_{0.05}$Sr$_{0.95}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ and K$_{0.1}$Sr$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ exhibit the entirely different oxygen permeation behavior at 750°C. As shown in Figure 6, K$_{0.05}$Sr$_{0.95}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ displays the highest initial oxygen permeation flux, which reaches about 0.75 ml min$^{-1}$.cm$^{-2}$, yet the gradual oxygen permeation decay along with time also occurs. Its oxygen permeation flux has fallen from 0.75 ml min$^{-1}$.cm$^{-2}$ to 0.43 ml min$^{-1}$.cm$^{-2}$ during 80 h oxygen permeation operation. It is interesting that K$_{0.1}$Sr$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ obtained the excellent intermediate-temperature oxygen permeation stability at 750°C for 120 h. It can be found that the initial oxygen permeation flux of K$_{0.1}$Sr$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ has a slightly down-trend from 0.69 ml min$^{-1}$.cm$^{-2}$ to 0.67 ml min$^{-1}$.cm$^{-2}$. Then, the stable oxygen permeation flux above 0.60 ml min$^{-1}$.cm$^{-2}$ can be maintained for K$_{0.1}$Sr$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ in 120 h long-term test. It should be mentioned that there is still a slight decrease in oxygen permeability for K$_{0.1}$Sr$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$, but the decay trend can be effectively inhibited. Rapid oxygen permeation degradation of most perovskite-based ceramic membranes at intermediate temperatures below 800°C always confuses the researchers. To address this issue, Liu et al. doped Ce into Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ to inhibit the heterogeneous nucleation at grain boundaries [32]. Ti$^{4+}$, Zr$^{4+}$, or Nb$^{5+}$ were also used as the dopants in perovskite oxides in order to optimize their phase stability at intermediate temperatures [33–35]. It should be mentioned that the improvement in intermediate-temperature stability from the above strategies is more and less at the expense of oxygen permeation flux. Little attention is paid to the balance between the stability and oxygen permeability. Here, K$_{0.1}$Sr$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ exhibits a “trade-off” between the intermediate-temperature stability and oxygen permeability, which enables the doping of K$^+$ to become an alternative means for intermediate-temperature oxygen permeable membranes. In the latter research, we mainly focused on oxygen permeation properties of K$_{0.1}$Sr$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$.

3.5. Rate-determining step and activation energy of K$_{0.1}$Sr$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ ceramic membranes

According to the related oxygen permeation theory, oxygen transfer passing through perovskite-base membranes proceeds by oxygen vacancy diffusion mechanism. Typically, oxygen molecules are firstly decomposed into oxygen ions, which is termed as the surface exchange process. Then oxygen ions permeate into the membrane matrix through perovskite lattice vacancies, which is called bulk diffusion process. Finally, oxygen ions recombine back to oxygen molecules on the permeated membrane surface. Among three procedures, the slowest step will control the whole oxygen permeation rate. The rate-determining step during oxygen permeation is very important because it concerns how to further improve the oxygen permeability for this new material. While the whole oxygen permeation is controlled by bulk diffusion, the Wagner equation, 

$$j_o = \frac{1}{16\pi L} \ln \frac{p_o}{p_2} \sigma_o \cdot d \ln p_2,$$

can be used to describe the oxygen permeation behavior, where the oxygen flux is directly proportional to 1/L. Otherwise, the oxygen permeation should be ascribed into the surface exchange process. For the same membrane, the bulk diffusion or surface exchange process relies on the membrane thickness, where L is always defined as the critical transition membrane thickness. If the membrane thickness is lower than L, the enhancement of oxygen flux by simply reducing membrane thickness is invalid and thus the surface activation catalysts should be used to accelerate the surface exchanging rate of oxygen molecules.

Figure 7 shows the oxygen permeation behavior of K$_{0.1}$Sr$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ with different thicknesses. It can be seen that the oxygen permeation flux of K$_{0.1}$Sr$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ increases with the decreased thickness from 700 to 950°C. For instance, K$_{0.1}$Sr$_{0.9}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ membrane with 1.5 mm thickness shows the oxygen

![Figure 6](image-url)  
Figure 6. Time-dependent oxygen permeation flux through K$_{0.1}$Sr$_{1-x}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ at 750°C (membrane thickness = 1.5 mm).
permeation flux of about 1.58 ml.min⁻¹.cm⁻² at 950°C. While its membrane thickness is reduced to about 0.7 mm, its oxygen permeation flux rapidly increases to 2.98 ml.min⁻¹.cm⁻². However, the growth trend in oxygen flux is slowing with the decrease of membrane thickness from 0.7 to 0.5 mm. Figure 8 presents the dependence of oxygen permeation flux of K₀.₁Sr₀.₉Co₀.₈Fe₀.₂O₃−δ on 1/L. As shown in Figure 8, the solid lines are the actual relationship between oxygen permeation flux and 1/L, and the assumed linear relationship of both is plotted using the dash lines. An approximate linear relationship between oxygen permeation flux and 1/L can be found when L = 1.5, 1.2, and 1.0 mm at 950, 850, and 750°C, which means that the oxygen permeation through K₀.₁Sr₀.₉Co₀.₈Fe₀.₂O₃−δ membrane above 0.7 mm can be attributed to the bulk diffusion controlled process. It can be found that the solid lines begin to deviate from the straight dashed line occurs when L = 0.7 mm. While the membrane thickness is decreased to 0.5 mm, the obvious nonlinear relationship between oxygen flux and 1/L can be observed. The experimental results showed that the surface exchanging process has become the rate-determining step below 0.7 mm. Therefore, the critical transition membrane thickness from bulk diffusion to surface exchange is about 0.7 mm.

Here, the surface exchange current model (SECM) is also adopted to check the rate-determining step of K₀.₁Sr₀.₉Co₀.₈Fe₀.₂O₃−δ [36,37]. Two membrane samples with 1.0 and 0.5 mm membrane thickness were selected to investigate their oxygen permeation process. According to SECM model, if there is a linear relationship between the oxygen permeation flux and (P₁/P₀)₀.₅−(P₂/P₀)₀.₅, the oxygen permeation is attributed to the surface exchanging controlled process. While the oxygen permeation flux is in direct proportion to ln(P₁/P₀), the oxygen permeation process is controlled by bulk diffusion. Here, two membrane

![Figure 7](image-url)  
**Figure 7.** Effects of the membrane thickness on oxygen permeation flux for K₀.₁Sr₀.₉Co₀.₈Fe₀.₂O₃−δ (He flow rate: 40 ml.min⁻¹; air flow rate: 100 ml.min⁻¹).

![Figure 8](image-url)  
**Figure 8.** Relationship of oxygen permeation flux of K₀.₁Sr₀.₉Co₀.₈Fe₀.₂O₃−δ and the reciprocal of membrane thickness (He flow rate: 40 ml.min⁻¹; air flow rate: 100 ml.min⁻¹).
samples with 1.0 and 0.5 mm membrane thickness were used to verify the SECM model. As for $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane ($L = 1.0$ mm), Figure 9(A, B) shows that its oxygen flux ($J_{O_2}$) has a linear relationship with $\ln(P_1/P_2)$, whereas $O_2$ is not proportional to $(P_1/P_0)^{0.5} - (P_2/P_0)^{0.5}$. The experimental result demonstrates that $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}$ sample with the membrane thickness of 1.0 mm is indeed controlled by bulk diffusion. For $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane with 0.5 mm thickness, its oxygen permeation flux is approximately proportional to $(P_1/P_0)^{0.5} - (P_2/P_0)^{0.5}$, and yet deviate from the linear relationship with $\ln(P_1/P_2)$ as shown in Figure 9(C, D). This fitting result based on SECM model demonstrates that the sample with

![Figure 9](image-url)  
**Figure 9.** Kinetic analysis of the oxygen permeation based on $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}$ with different thickness. (A) The oxygen permeation flux of $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}$ versus $(P_1/P_0)^{0.5} - (P_2/P_0)^{0.5}$ when $L = 1.0$ mm; (B) the oxygen permeation flux of $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}$ versus $\ln(P_1/P_2)$ when $L = 1.0$ mm; (C) the oxygen permeation flux of $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}$ versus $\ln(P_1/P_2)$ when $L = 0.5$ mm; (D) the oxygen permeation flux of $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}$ versus $\ln(P_1/P_2)$ when $L = 0.5$ mm. $P_1$ denotes oxygen partial pressure at feed side; $P_2$ denotes oxygen partial pressure at permeate side ($P_1 > P_2$); $P_0$ denotes the standard atmospheric pressure. He flow rate, 40 ml min$^{-1}$; air flow rate, 100 ml min$^{-1}$.

![Figure 10](image-url)  
**Figure 10.** Arrhenius plots of the oxygen permeation process based on $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes with different thickness.
0.5 mm thickness should belong to the typical surface exchange reaction. Therefore, while the membrane thickness of $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-δ}$ sample is decreased to 0.5 mm, it is ineffective to improve its oxygen permeation flux by further reducing the membrane thickness. The surface modification treatment with some highly active catalysts should be considered when designing practical membrane modules [38,39].

Figure 10 presents the activation energy of oxygen permeation based on $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-δ}$ (0.5 and 1.0 mm). It can be found that the activation energy of $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-δ}$ membrane (0.5 mm) is about 48.37 kJ mol$^{-1}$ which is slightly higher than that of the membrane (1.0 mm). Compared with some reported membrane samples such as $Ba_{0.2}Sr_{0.5}Ca_{0.8}Fe_{0.2}O_{3-δ}$ [40], $Ba_{0.2}Sr_{0.5}Ca_{0.8}Fe_{0.2}O_{3-δ}$ [41], and $Ba_{0.33}Sr_{0.33}Ca_{0.8}Fe_{0.2}O_{3-δ}$ [26], $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-δ}$ exhibits the lower activation energy. Hence, the suitable doping of $K^+$ in SCFO matrix can obtain an excellent balance between oxygen permeation flux and structural stability.

4. Conclusions

To address the stability issue, $K_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-δ}$ perovskite-based oxygen permeation membrane materials were developed by optimizing the doping content of $K^+$. Effects of $K^+$ doping content on phase structure, surface morphology, the oxygen flux, and medium-temperature stability of $K_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-δ}$ were firstly investigated. While $K^+$ doping content in A-site lattice of $K_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-δ}$ is no more than 20%, $K_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-δ}$ exhibits the pure cubic perovskite structure. A small amount of doping of $K^+$ in $SrCo_{0.8}Fe_{0.2}O_{3-δ}$ is favorable to enhance their oxygen permeation flux, but excessive doping of $K^+$ is disadvantageous to their oxygen permeability, which is possibly referred to the balance of $K$–O bond energy and oxygen vacancies. Compared to oxygen permeation flux, the structural stability and intermediate-temperature stability of $K_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-δ}$ can be obviously improved via the doping of $K^+$. The doping of $K^+$ not only inhibits the cracking of the membrane disks, but also improves their intermediate-temperature oxygen permeation stability. The $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-δ}$ membrane offers a steady oxygen flux of above 0.61 ml min$^{-1}$ cm$^{-2}$ at 750°C. Oxygen permeation kinetic analysis of $K_{0.1}Sr_{0.9}Co_{0.8}Fe_{0.2}O_{3-δ}$ demonstrates that the bulk diffusion is the rate-determining step while the membrane thickness is higher than 0.7 mm. If the membrane thickness is thinner than 0.7 mm, the surface exchange reaction will become the rate-determining step.

Disclosure of potential conflicts of interest

No potential conflict of interest was reported by the author(s).

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