Stability of sulfate doped \( \text{SrCoO}_3-\delta \) MIEC membrane

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**Abstract**

A sulfate doped \( \text{SrCoO}_3-\delta \) (SC) mixed ionic-electronic conducting (MIEC) oxide, \( \text{SrCo}_{0.97}\text{Sr}_0.03\text{O}_3-\delta \) (SCS), was prepared to study the dependence of its stability on the incorporation of sulfate group into perovskite lattice. The high-temperature cubic perovskite phase can be stabilized down to room temperature by replacing 3% of cobalt-sites with sulfur. However, permeation experiments show that oxygen permeation fluxes through SC and SCS membranes experienced similar degradation processes at 850 °C. Hysteresis loops of oxygen permeation fluxes appear on the both membranes indicate a phase transition from cubic to hexagonal during cooling/heating circle of oxygen permeation tests. The results of permeation experiments, annealing treatments in an air or helium atmosphere and the EDS analysis show that more \( \text{SrSO}_4 \) particles are enriched on the sweep side surface. A mechanism analysis on the sulfate group migration from the membrane bulk to surfaces was proposed to help understanding the experimental results. It is concluded that the sulfate group can migrate outside of perovskite lattice and reach to the gas–solid interfaces, so the stabilization function of sulfate to the cubic perovskite phase loses easily as the sulfate doped perovskite membrane encountering annealing treatments or oxygen partial pressure gradients.

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1. Introduction

Mixed ionic-electronic conducting (MIEC) membrane technology has received increasing attentions from academies and industries for pure oxygen production [1–9] or combined with oxyfuel for \( \text{CO}_2 \) capture [10–12], because the new technology exhibits much more energy and investment savings compared with the traditional oxygen separation methods, i.e. cryogenic distillation and pressure swing adsorption (PSA). MIEC membranes can be attractive reactors for selective oxidation or reduction reactions with high selectivity or conversion [13–17]. Cobalt-containing perovskite oxides with higher oxygen ionic and electronic conductivity are potential MIEC membrane materials and solid oxide fuel cells (SOFCs) cathode materials, and have been widely investigated because of their high oxygen permeability and good catalytic activity toward oxygen reduction reactions [18–23]. Among the cobalt-containing perovskite oxides, strontium cobaltite \( \text{SrCoO}_3-\delta \) (SC) perovskite is one kind of promising MIEC membranes and SOFCs cathodes after Sr and/or Co sites doped by proper metal ions. For the undoped SC perovskite oxide, phase change happens during the fabrication process or under working conditions. This material may display different structures, such as 2-H type hexagonal, brownmillerite, rhombohedral, or cubic under various conditions, for instance, oxygen partial pressure, temperature and synthesis method [24–27]. Among these phase structures, SC with the cubic perovskite structure shows the highest electronic and oxygen ionic conductivity [28,29]. Therefore, the cubic structure is preferred as it is used as the MIEC membrane or SOFCs cathode for oxygen separation or oxygen activation. In air, SC changes from a cubic phase to a hexagonal phase with the 2H-BaNiO\textsubscript{3} type structure as temperature lower than 900 °C [21,30]. The hexagonal phase is almost non-oxygen permeable due to the ordered oxygen vacancies in this structure. The structural instability (phase change from cubic to hexagonal) thus limits its applications as a SOFCs cathode or MIEC membrane.

In order to inhibit the phase transition and stabilize the cubic perovskite structure down to room temperature, metal cations were used to partially replace Sr and/or Co ions of SC oxide. Rare earth and alkaline earth elements are extensively used to partially substitute Sr, while metal elements in the third, fourth and fifth periods are often incorporated into Co-site to stabilize the high-temperature cubic phase to room temperature. Lanthanide doped SC oxides, \( \text{La}_{x}\text{Sr}_{1-x}\text{CoO}_3-\delta \) (LSC, \( \text{Ln} = \text{La, Pr, Nd, Sm and Gd} \)) as the SOFCs cathode materials have been widely studied. Gwon et al. systematically investigated the effects of La in \( \text{Ln}_{x}\text{Sr}_{1-x}\text{CoO}_3-\delta \) cathodes on the structure, electrical properties, and electrochemical performance [28]. They found that the electrical conductivities of \( \text{La}_{x}\text{Sr}_{1-x}\text{CoO}_3-\delta \) in air increase with the doping
amount of lanthanum elements as $x$ is smaller than 0.4. Many researchers have investigated the phase structure stability and oxygen permeability of the SC-based materials with Co-site doped by various cations, such as Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Cr$^{3+}/4+$, Fe$^{3+}/4+$, Al$^{3+}$, Ga$^{3+}$, In$^{3+}$, Ti$^{4+}$, Zr$^{4+}$, Sn$^{4+}$, Ce$^{4+}$, V$^{5+}$, Nb$^{5+}$, and Ta$^{5+}$. Nagai et al. found that the perovskite stability upon the substituting cations for (La$_{0.1}$Sr$_{0.9}$)CoO$_{3-\delta}$ and Sr(Co$_{0.9}$X)$_{0.1}$O$_{3-\delta}$ (where $X$ is Ni, Cu, Zn, Cr, Fe, Al, Ga, In, Ce, Ti, Zr, Sn, V, and Nb) increases according to the sequence of Ni, Cu, Zn, In, Ce < Cr, Al, Ga, Zr, Sn, V < La < Fe < Ti < Nb. And they observed that the oxygen permeability at 900 °C decreases as follow, Sr(Co$_{0.9}$Nb)$_{0.1}$O$_{3-\delta}$ ≥ SrCoO$_{3-\delta}$ > Sr(Co$_{0.9}$Fe)$_{0.1}$O$_{3-\delta}$ > Sr(Co$_{0.9}$Fe)$_{0.2}$O$_{3-\delta}$ > SrCo$_{0.9}$S$_{0.1}$O$_{3-\delta}$ [21].

Recently, a novel doping approach was proposed to stabilize the cubic perovskite structure of SrCoO$_{3-\delta}$ by incorporating oxyanions, including borate, silicate, phosphate and sulfate, into perovskite lattice [31-35]. Slater et al. successfully incorporated sulfate and phosphate into SC lattice and stabilize the SC cubic perovskite structure at room temperature [32]. They also incorporated borate and phosphate into Ba$_{1-x}$Sr$_x$CoO$_{3-\delta}$ cathode materials to improve the structural stability of the cathodes at intermediate temperatures [34]. Zhou et al. investigated a phosphate doped perovskite, SrCo$_{0.85}$Fe$_{0.15}$O$_{3-\delta}$, and observed that the incorporation of phosphate can prevent oxygen vacancy ordering at temperatures higher than 600 °C both in air and atmospheres with lower oxygen partial pressure [35].

The aforementioned researches verified that the incorporation of oxyanions can prevent the Sr–Co–O system from oxygen vacancy ordering and stabilize the cubic perovskite phase. However, in our previous investigation on the degradation of oxygen permeation flux of MIEC membranes at low temperature (350–650 °C), we found that tiny sulfur or silicon impurities coming from raw chemicals would migrate from membrane bulk to membrane surfaces, and enrich on the sweep side surfaces as sulfates or silicates, respectively. The enrichment of sulfur or silicon impurities on membrane surfaces blocks the oxygen exchange reactions and lead to the degradation of oxygen permeation flux upon long-term operation [36-38]. The sulfur content is higher up to 7.5 at% after the BaCo$_{0.97}$Fe$_{0.03}$O$_{3-\delta}$ membrane operated under an air/He gradient for 100 h at 650 °C [36]. We also found that the enrichment of sulfur impurities on the Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ (BSFC) membrane surfaces has large contribution to the degradation of oxygen permeation flux at low temperature [38]. In addition, other researchers also found that sulfur has poisoning effect on perovskite membranes. Diniz da Costa et al. found that the sulfur containing binders would result in lower oxygen flux of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ (BSFC) hollow fiber membrane due to the formation of non-ionic conducting domains of Co$_2$O$_4$, SrSO$_4$, and BaSO$_4$ within the BSFC structure [39]. Tan et al. found that the oxygen permeability of Lao$_{0.1}$SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ (LSCF) hollow fiber membrane decreases significantly or even completely disappear after exposing to SO$_2$ because of the decomposition of the LSCF material and the formation of SrSO$_4$ [40].

However, it is unclear whether the perovskite oxides doped by oxyanions also show the enrichment of impurities on membrane surfaces during oxygen separation. Additionally, the structural stability of the oxygenic doped perovskite membrane is unclear under an oxygen chemical potential gradient at working temperatures. Therefore, in this paper a sulfated doped SrCoO$_{3-\delta}$ MIEC membrane was investigated as an example, and its oxygen permeation behavior, structural stability and migration mechanism of sulfate groups were discussed.

2. Experimental

2.1. Preparation of powder and membranes

SrCo$_{0.97}$S$_{0.03}$O$_{3-\delta}$ (SCS) powder was synthesized by using a combined ethylenediamine tetraacetic (EDTA) acid and citric acid complex method. Stoichiometric amounts of metal nitrates Sr(NO$_3$)$_2$ (≥ 99.0%) and Co(NO$_3$)$_2$ · 6H$_2$O (≥ 98%) were dissolved in deionized water, then the EDTA acid and citric acid were introduced in the solution. The molar ratio of total metal ions: EDTA acid: citric acid was 1: 1: 1.5. Stoichiometric amount of (NH$_4$)$_2$SO$_4$ (≥ 99.0%) was introduced in the above solution after the pH value was adjusted to 8–10 by NH$_3$·H$_2$O. Then the solution was heated and stirred on a hot pot to evaporate water till a dark purple gel formed. The gel was transferred into an evaporating dish and heated to self-combustion by an electric stove. The resultant ash was calcined at 950 °C for 5 h to obtain the SCS powder. The SrCo$_{3-\delta}$ (SC) powder was synthesized by the same method as that for the SCS powder. The as-prepared powders were compressed into disks in a stainless steel mold with diameter of 18 mm under a pressure of 200–300 MPa. The green disks were sintered at 1200 °C for 3 h with heating/cooling rates of 2 °C/min. The as-sintered disks were polished by using 500-mesh waterproof sandpaper to 0.5 mm in thickness before oxygen permeation experiments.

2.2. Measurements of oxygen permeation

Silver rings made of silver wire (＞99.99%) with diameter of 1.5 mm were used to seal membranes at 961 °C. The effective membrane areas for oxygen permeation were around 1.0 cm$^2$. Operation temperatures were controlled by a microprocessor temperature controller (AI-708, Xiamen Yuguang Electronics Technology Research Institute, China) within ± 1 °C with a K-type thermocouple. Dry synthesized air (O$_2$: 21 vol%, 150 mL min$^{-1}$) and high purity helium (50 mL min$^{-1}$) were used as feed and sweep gases, respectively. The flow rates of the gases were controlled by mass flow controllers (D07-7A/ZM, Beijing Jiazhang Machine Factory, China) and measured at 25 °C and one standard atmospheric pressure in this study. All the gases passed through cylinders (Ø 50 mm × 300 mm) filled with 50 vol% KOH pellets and 50 vol% 4A zeolite granules before introducing into the permeation cell. Effluents were analyzed by a gas chromatography (Agilent...
Oxygen permeation fluxes through the membranes were calculated based on the following equation,

\[ J_{O_2} = \left( C_{O_2} - C_{N_2} \times \frac{V_{O_2}}{V_{N_2}} \times \sqrt{\frac{M_{N_2}}{M_{O_2}}} \right) \times F/S \]  

where \( C_{O_2} \) and \( C_{N_2} \) are the concentrations of oxygen and nitrogen in the effluents, respectively. \( V_{O_2} \) and \( V_{N_2} \) are the volume percentages of oxygen and nitrogen in feed gas, respectively. \( M_{O_2} \) and \( M_{N_2} \) are the molecular masses of oxygen and nitrogen molecules, respectively. \( F \) is the flow rate of the effluent. \( S \) is the effective membrane area. The oxygen leakages due to imperfect sealing were no more than 2% for all the oxygen permeation experiments, and were subtracted when calculating the permeation fluxes.

2.3. Characterizations

Phase structure of the SCS and SC disks was determined by X-ray diffraction (XRD, Rigaku D/Max-2500) with Cu K\( \alpha \) radiation. Membrane morphologies were observed by scanning electron microscopy (SEM, Quanta 200FEG, FEI Company) operated at 20 kV. The energy dispersive X-ray spectroscopy (EDS) was operated at a lower voltage of 10 kV to obtain the elemental composition information on the membrane surfaces.

3. Results and discussion

3.1. Crystal structures and microstructures of the as-sintered disks

Fig. 1 shows the XRD patterns of the as-prepared SC and SCS disks at room temperature. The SC disk shows a 2H-BaNiO\(_3\) type hexagonal structure. As for the SCS disk, except for a small amount of unknown impurities (the peaks at \( 2\theta \) 42° and 48.3°), the cubic perovskite phase was observed. This stabilization function to the cubic framework through S\(^6^+\) doping can be attributed to a partial reduction of Co\(^{4+}\) to Co\(^{3+}\), thus increasing the perovskite B cation size, and hence reducing the tolerance factor [31]. Fig. 2 shows the SEM images of the as-prepared SC and SCS disks. There is no pore on the surface of the SC disk, and the grain size of SC is in the range of 10–50 \( \mu \)m (Fig. 2a); while some blind pores with diameter of 1–2 \( \mu \)m appear in the cross-section, and a lamellar-type
Fig. 4. Effects of cooling/heating circle on the oxygen permeation fluxes of the SC and SCS membranes. (a) SC, (b) SCS and (c) SCS after 40 h on-stream at 850 °C. The open and solid symbols show the cooling and heating steps, respectively.

microstructure was observed (Fig. 2b). This lamellar-type microstructure indicates that the SC oxide changed to a hexagonal structure during the cooling step of sintering. This deduction coincides with the XRD result. The morphology of SCS disk is significantly different from that of SC disk. There are many pores in the surface of the SCS disk, and the grain size is in the range of 5–10 μm (Fig. 2c), that implies the doping of SO$_4^{2-}$ in SC lattices inhibits the ceramic sintering. The cross-sectional morphology is typical in MIEC ceramics, and no lamellar-type microstructure was observed (Fig. 2d). SrSO$_4$ particles marked by arrows were verified by EDS analysis in the insert image of Fig. 2c. This observation indicates that not all SO$_4^{2-}$ ions incorporated into the perovskite lattice, and some SO$_4^{2-}$ ions combined with Sr$^{2+}$ to form SrSO$_4$ particles. However, the amount of SrSO$_4$ is too low to be detectable by XRD.

3.2. Oxygen permeation of the membranes

The SC oxide has the cubic perovskite structure if the temperature is higher than 900 °C [21,30]. Therefore, as the SC membrane was operated at 850 °C, the phase transition from cubic to hexagonal would take place. The hexagonal phase has much lower oxygen ionic conductivity than that of the cubic phase, so the time-dependent oxygen permeation flux of this material can indicate the phase transition process. Fig. 3 shows the time-dependent oxygen permeation fluxes of SC and SCS membranes at 850 °C. The initial oxygen permeation flux of SC is higher than that of SCS membrane. However, the oxygen permeation fluxes of the two membranes almost decrease to zero after ~30 h on-stream. This result indicates that the cubic perovskite structure of SCS membrane maybe convert back to the hexagonal structure during the oxygen permeation test proceeding. Cooling and heating circles of the oxygen permeation experiment can effectively reflect a reversible phase transition process [29]. Therefore, the circles of the oxygen permeation experiments on SC and SCS were carried out by decreasing the operation temperature from 950 to 750 °C and then raising it from 750 to 950 °C at a cooling/heating rate of 2 °C/min. As shown in Fig. 4a, an obvious hysteresis effect appeared during the heating step, which indicates a phase transition taking place during the cooling/heating circle. The oxygen permeation fluxes of SC and SCS membranes all decrease with temperature from 950 to 750 °C. During the heating process, the oxygen permeation flux of SC membrane drops continuously until the temperature is high up to 900 °C. This phenomenon indicates that the crystal structure transition from cubic to hexagonal phase takes place blow 900 °C, and then the material restores the cubic structure gradually as the temperature is higher than 900 °C. As the temperature goes back to 950 °C, the material recovers its cubic structure since the oxygen permeation flux returns to the initial level. In contrast to SC, the hysteresis degree of the SCS membrane is much weaker than that of SC, as shown in Fig. 4b. This result indicates that the incorporation of sulfate into the lattice of SC has a stabilization function on keeping the cubic structure. However, if the SCS membrane was experienced a 40 h on-stream at 850 °C and then performed for the cooling/heating circle, a similar hysteresis phenomenon as that of SC was observed, as shown in Fig. 4c. This result implies that SO$_4^{2-}$ ions have migrated outside of the perovskite lattice after 40 h on-stream. Thus, the stabilization function of SO$_4^{2-}$ ions to the cubic perovskite structure is limited and irreversible under the cooling/heating circles.

3.3. Characterization of the spent membranes

The crystal structure of SC and SCS membranes after oxygen permeation test were determined by XRD. As shown in Fig. 5a, the cubic phase of SCS has completely transformed to the hexagonal phase after 40 h oxygen permeation at 850 °C. In addition, the peaks of SrSO$_4$ were also observed on the both surfaces of SCS, as shown in Fig. 5b. This result indicates that the SO$_4^{2-}$ migrates outside of the perovskite lattice and combines with Sr$^{2+}$ to form SrSO$_4$, meanwhile the cubic phase convert back to the hexagonal phase. Fig. 6 shows the SEM images of the two sides of the SCS
membrane after 40 h on-stream. SrSO₄ particles were observed on both surfaces (marked by arrows), and the sulfur content on the sweep side surface is 3.90 at%, which is higher than that on the feed side surface (2.09 at%).

3.4. Analysis of the sulfur migration

To help understand the migration of sulfur, the SCS disks were treated in flowing air and helium (50 mL min⁻¹) at 850 °C for 40 h.

Table 1
Elemental compositions detected by EDS at 10 kV of the as-prepared membrane and the membranes treated in flowing air and helium, respectively, at 850 °C for 40 h. Oxygen was not included.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Sr (at%)</th>
<th>Co (at%)</th>
<th>S (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared</td>
<td>46.0</td>
<td>52.0</td>
<td>2.1</td>
</tr>
<tr>
<td>Treated in air</td>
<td>49.4</td>
<td>45.8</td>
<td>4.9</td>
</tr>
<tr>
<td>Treated in helium</td>
<td>49.3</td>
<td>5.8</td>
<td>44.9</td>
</tr>
</tbody>
</table>

membrane after 40 h on-stream. SrSO₄ particles were observed on the both surfaces (marked by arrows), and the sulfur content on the sweep side surface is 3.90 at%, which is higher than that on the feed side surface (2.09 at%).

3.4. Analysis of the sulfur migration

To help understand the migration of sulfur, the SCS disks were treated in flowing air and helium (50 mL min⁻¹) at 850 °C for 40 h,
respectively. After the treatment, SrSO₄ particles were observed on the surfaces of the disks, as shown in Fig. 7. The amount of SrSO₄ particles on surfaces for the disk treated in the flowing helium is more and bigger than that of treated in flowing air. EDS analysis shows that the sulfur contents of the disks treated in flowing air and helium are about 5 and 45 at%, respectively, as listed in Table 1. The sulfur content of the as-prepared SCS membrane is provided for comparison. The whole surface of the disk treated in helium is almost covered by the SrSO₄ particles indicated by the Sr/S atomic ratio of about 1. The above results show that the migration of sulfur element from perovskite lattice to surfaces is significant affected by the oxygen partial pressure. Although the microscopic migration mechanism is difficult to be disclosed, a simple analysis on the experimental results is meaningful to help the understanding of the sulfur migration mechanism in perovskite lattice. As the sulfur elements migrate outside of the perovskite lattice during the treatment in flowing gases, the migration driving force is the difference in chemical potential of sulfur element between the perovskite lattice and that of the gas–solid interfaces.

The above experiments reveal that at the gas–solid interface, the chemical potential of sulfur element is related to the oxygen partial pressure. Fig. 8 is drawn to illustrate how the oxygen partial pressure affects the sulfur migration. When the membrane was sintered at 1200 °C and then treated in air at 850 °C, the chemical potential of sulfur element in perovskite lattice (μ_S/Latt) is higher than that at air–solid interface (μ_S/Interf), so the sulfur element migrates from the membrane bulk to surfaces, as illustrated by Fig. 8a. When the membrane was treated in helium, similarly, the chemical potential of sulfur element in perovskite lattice (μ_S/Latt) is much higher than that at helium–solid interface (μ_S/Interf), so the sulfur element also migrates from the membrane bulk to surfaces, as illustrated by Fig. 8b. Additionally, more sulfur element was enriched on the surface of the membrane treated in helium (44.9 at%) than that of treated in air (4.9 at%), which indicates that μ_S/Interf is higher than μ_S/Interf at 850 °C. Therefore, the chemical potential difference of sulfur element between perovskite lattice and air–solid interface (μ_S/Latt − μ_S/Interf) is smaller than that of between perovskite lattice and helium–solid interface (μ_S/Latt − μ_S/Interf). If the membrane is operated for oxygen permeation, sulfur element migrates from the membrane bulk to the both surfaces, as illustrated by Fig. 8c. Therefore, sulfur element was observed on the both surfaces, and it on helium side (i.e. sweep side) surface was higher than that on air side (i.e. feed side) surface. This result coincides with our previous findings on the migration of tiny silicon and sulfur impurities in BaCe₀.₁Co₀.₄Fe₀.₅O₃–δ and BSCF perovskite membranes [36–38]. From the above discussion, it can be inferred that the sulfate group can stabilize the cubic perovskite structure of the SC oxide but the stabilization function loses easily as encountering annealing treatments or oxygen partial pressure gradient.

4. Conclusions

In summary, the cubic perovskite structure of SrCoO₃–δ is successfully kept down to room temperature after incorporating a small amount of sulfate. However, the oxygen permeation flux of SCS membrane degraded with time at 850 °C. The hysteresis loops of oxygen permeation fluxes in the cooling/heating experiments and the XRD patterns after 40 h oxygen permeation experiments demonstrate that the doping of sulfate in SC cannot completely inhibit the phase change from cubic to hexagonal. It was found that the sulfate groups which have incorporated in SC lattice during high temperature calcining can migrate outside of the perovskite lattice and combine with strontium ions to form SrSO₄ during the oxygen permeation process or annealing treatments. The content of sulfur on sweep side is higher than that on the feed side owing to the chemical potential of sulfur element at the gas–solid interface increases with the oxygen partial pressure. In a word, the doping of sulfate in SC perovskite can stabilize the cubic perovskite structure down to room temperature but the stabilization function loses easily as encountering annealing treatments or oxygen partial pressure gradient, so the sulfate doped materials are improper to be used as MIEC membranes or SOFCs cathodes from a viewpoint of stability.

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