A novel zincum-doped perovskite-type ceramic membrane for oxygen separation

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1. Introduction

Oxygen is ranked among the top five in the production of commodity chemicals in the world [1]. How to obtain cheap, pure oxygen is a very important issue in industry. Commercial oxygen is currently produced by cryogenic distillation and pressure swing adsorption (PSA), which are very costly technologies. Since Teraoka et al. first reported the oxygen permeation through a perovskite membrane based on La1−xSrxCoO3−δ with constant valence (Zr4+, Ga3+, Al3+) [7–11] were used to partially substitute the reducible B-site ions (Co4+, Fe3+, Zr4+) [2,3] with 0 ≤ x ≤ 0.2 were synthesized by combining citric acid and ethylene-diamine-tetraacetic acid (EDTA) complexing method. X-ray diffraction (XRD) patterns show that the BaCo0.4Fe0.4Zr0.2O3−δ ceramic oxide exhibits a pure cubic perovskite structure. Oxygen temperature-programmed desorption (O2-TPD) profile indicates that BaCo0.4Fe0.4Zn0.2O3−δ possesses a good phase reversibility. An oxygen permeation flux of 0.65 ml/min cm2 was obtained at 950 °C and a single activation energy of 67 kJ/mol was observed for the oxygen permeation in the temperature range of 600–950 °C. No decline was found during more than 100 h oxygen permeation.

2. Experimental

The oxide powders were synthesized by combining the ethylene-diamine-tetraacetic acid (EDTA) and citric acid complexation technique [21]. The as-synthesized powders were pressed to disk-type membranes under a pressure of 18–24 MPa in a stainless steel module with a diameter of 16 mm. The green disks were sintered at 1000 °C for 10 h. The densities of the sintered membranes were determined by the Archimedes method using ethanol. Only those membranes with relative densities higher than 95% were chosen for the oxygen permeation studies.

The phase structure was characterized by X-ray diffraction (XRD, Rigaku D-Max/RR). Oxygen temperature-programmed desorption (O2-TPD) was performed on Micromeritics AutoChem II 2920™. The purity of all gases (O2, H2, He, Ar) used in O2-TPD and the permeation studies was 99.999%. Before the oxygen desorption,
The Zr⁴⁺ ion is too large to enter easily into the perovskite structure, the membrane disks was about 0.60–0.80 cm². Permeation studies were performed held at this temperature for 3–5 h to densify the sealing. The effective surface area of using a thermal conductivity detector (TCD). In order to investigate the reversibility of oxygen adsorption and desorption, the samples after O₂-TPD were pre-treated again in flowing oxygen at 950 °C, and then the next O₂-TPD was performed again. The oxygen permeation was performed in a self-made high temperature permeator, as shown in Fig. 1. The as-synthesized disk-type membrane was polished with 1000 mesh SiC sand paper on both surfaces. A gold paste was used to seal the membrane disk onto the dense quartz tube. The sidewall of the disk was also covered with 1000 mesh SiC sand paper on both surfaces. A gold paste was used to seal the membrane disk onto the dense quartz tube. The sidewall of the disk was also covered with the different sides of the membrane disk. The flow rates 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 mixtures of oxygen and He was used as the carrier gas. The amount of desorbed oxygen was detected by a soap film meter.

\[ J_{\text{O}_2} \text{ (ml/ min cm}^2\) = \frac{C_{\text{O}_2} - C_{\text{N}_2}}{S} \times F \]  

(1)

We should point out that the oxygen leakage is lower than 2% during our oxygen permeation. The oxygen permeation flux was then calculated as follows:

\[ J_{\text{O}_2} \text{ (ml/ min cm}^2\) = \frac{(C_{\text{O}_2} - C_{\text{N}_2}) \times F}{S} \]  

(2)

where \(C_{\text{O}_2}\) and \(C_{\text{N}_2}\) are the oxygen and nitrogen concentrations calculated from GC calibration, \(F\) is the total flow rate of the outlet on the sweep side, which was measured by a soap film meter, \(S\) is the membrane area. The setup of the permeation cell and the calculation of oxygen permeation flux were presented elsewhere [22].

3. Results and discussion

Fig. 2 shows the XRD patterns of the series of BaCo₄Fe₀.₄Zn₀.₂Zr₀.₂−ₓO₃₋ₓ powders with 0 ≤ x ≤ 0.2. All oxides were prepared by the same preparation procedure, i.e. by the combined EDTA-citric acid complexing method. The BaCo₄Fe₀.₄Zn₀.₂Zr₀.₂O₃₋ₓ displayed two phases: one phase is perovskite and the other is ZrO₂. However, when Zr was partially replaced by Zn, the peak of the ZrO₂ phase became weaker. When Zr was completely substituted by Zn, only the pure perovskite phase was found in the XRD pattern. Previously Tong et al. reported the synthesis of BaCo₄Fe₀.₄Zn₀.₂Zr₀.₂O₃₋ₓ with a pure perovskite structure, but his preparation method was very complex [7]. Caro et al. [23] reported that the radius of the Zr⁴⁺ ion is too large to enter easily into the perovskite structure, thus foreign phases can form. Lu et al. [24] also found an impurity phase in BaCo₄Fe₀.₄Zn₀.₂Zr₀.₂O₃₋ₓ. However, BaCo₄Fe₀.₄Zn₀.₂Zr₀.₂O₃₋ₓ can easily form a pure perovskite structure, which is due to the fact that the Zn²⁺ ion (ionic radius = 74 pm) is much smaller than the Zr⁴⁺ ion (ionic radius = 86 pm). Therefore, the pure perovskite phase BaCo₄Fe₀.₄Zn₀.₂Zr₀.₂O₃₋ₓ was used in this study.

The O₂-TPD technique provides not only an effective way to characterize the oxygen absorption/adsorption properties but also an indirect evidence for the structure stability of the ceramic oxides. Fig. 3 shows the profiles of the O₂-TPD for BaCo₄Fe₀.₄Zn₀.₂Zr₀.₂O₃₋ₓ. A single oxygen desorption peak was observed in the low temperature zone from 200–500 °C. The oxygen desorption peak in the low temperature zone is due to the reduction of Co⁴⁺/Fe⁴⁺ to Co³⁺/Fe³⁺. However, the oxygen desorption peak in the high temperature zone is related to the reduction of Co³⁺/Fe³⁺ to Co²⁺/Fe²⁺, which lead to a larger expansion of the lattice and the perovskite structure can be destroyed because of a big difference in the ionic radii between Co³⁺/Fe³⁺ and Co²⁺/Fe²⁺ [7]. For a good structure stability it is recommended, therefore, to avoid the reduction of Co³⁺/Fe³⁺ to Co²⁺/Fe²⁺. For the BaCo₄Fe₀.₄Zn₀.₂Zr₀.₂O₃₋ₓ, no oxygen desorption peak was found in the high temperature zone, which indicates that the introduction of Zn²⁺ can restrain the reduction of the Co³⁺ and/or Fe³⁺ ions. From the multi-run O₂-TPD profiles it can be seen that BaCo₄Fe₀.₄Zn₀.₂Zr₀.₂O₃₋ₓ possesses a good phase reversibility for oxygen adsorption and desorption. After the multi-run O₂-TPD, the sample was characterized by XRD, as shown in Fig. 4. It can be seen that the perovskite structure was kept, which indicates that BaCo₄Fe₀.₄Zn₀.₂Zr₀.₂O₃₋ₓ exhibits an excellent structure stability and reversibility.

Fig. 5 shows the oxygen permeation fluxes as a function of temperature under an Air/He oxygen gradient. The oxygen permeation flux:

\[ J_{\text{O}_2} \text{ (ml/ min cm}^2\) = \frac{(C_{\text{O}_2} - C_{\text{N}_2}) \times F}{S} \]  

(3)

where \(C_{\text{O}_2}\) and \(C_{\text{N}_2}\) are the oxygen and nitrogen concentrations calculated from GC calibration, \(F\) is the total flow rate of the outlet on the sweep side, which was measured by a soap film meter, \(S\) is the membrane area. The setup of the permeation cell and the calculation of oxygen permeation flux were presented elsewhere [22].

![Fig. 2. XRD patterns of BaCo₄Fe₀.₄Zn₀.₂Zr₀.₂O₃₋ₓ ceramic oxide.](image-url)

![Fig. 3. Multi-run O₂-TPD profiles of BaCo₄Fe₀.₄Zn₀.₂Zr₀.₂O₃₋ₓ ceramic oxide.](image-url)
Helium flow rate = 30 ml/min.

run O2-TPD.

gen permeation through the BaCo0.4Fe0.4Zn0.2O3 mixed conducting membranes. The single activation energy for oxygen is an important feature for a good stability of oxygen permeation through the membrane.

Temperature dependence of oxygen permeation flux and activation energy for BaCo0.4Fe0.4Zn0.2O3 disk membrane: O2-TPD profiles.

Fig. 4. XRD patterns for the fresh BaCo0.4Fe0.4Zn0.2O3 disk membrane and the sample after multi-run O2-TPD.

Fig. 5. Temperature dependence of oxygen permeation flux and activation energy for BaCo0.4Fe0.4Zn0.2O3 disk membrane. L = 1.0 mm, Air flow rate = 150 ml/min, Helium flow rate = 30 ml/min.

Fig. 6. Relationship between oxygen permeation fluxes for BaCo0.4Fe0.4Zn0.2O3 disk membrane and oxygen partial pressure gradient \( \ln(P_h/P_l) \). L = 1.0 mm, Temperature = 900 °C, Air flow rate = 150 ml/min.

Flux increases with increasing temperatures from 600 to 950 °C, an oxygen permeation flux of 0.64 ml/cm² min was obtained at 950 °C. Kruidhof et al. [25] and Qiu et al. [26] reported that some perovskite membranes transform from the oxygen vacancies disorder state to oxygen vacancies order state when the temperature decreases, which leads to a sharp decrease of the oxygen permeation flux. However, our oxygen permeation flux curves do not show such sudden change which means that no oxygen vacancies order/disorder transformation takes place during decreasing the temperature from 950 to 600 °C. Another factor for evaluating the oxygen permeability of mixed conducting membranes is the activation energy for oxygen permeation. From the Arrhenius plot of oxygen permeation in Fig. 5, the activation energy for oxygen permeation of 67 kJ/mol was found. Furthermore, a single activation energy in the temperature range of 600–950 °C was observed. Tong et al. [7] reported that a single activation energy is an important feature for a good stability of oxygen permeation through the mixed conducting membranes. The single activation energy for oxygen permeation through the BaCo0.4Fe0.4Zn0.2O3 disk membrane can be interpreted by the structural stability characterized by the XRD patterns and O2-TPD profiles.

\[
J_0 = \frac{RT\sigma_e\sigma_i}{16F^2(\sigma_e + \sigma_i)L} \ln \left( \frac{P_h}{P_l} \right) 
\]

where \( R \) is the gas constant; \( F \) is the Faraday constant; \( T \) is the temperature; \( L \) is the thickness of the membrane; \( P_h \) is the oxygen partial pressure on the air side; \( P_l \) is the oxygen partial pressure on the helium side, which depends on the oxygen permeation flux and the helium flow rate. \( \sigma_e \) and \( \sigma_i \) are the electronic and ionic conductivity, respectively. For a constant membrane thickness \( L \), the oxygen permeation flux \( J_0 \) (related against \( \ln(P_h/P_l) \)) is linear and goes through the origin of the coordinates if the limiting step of the oxygen permeation is bulk diffusion. In our experiment it was found that the oxygen permeation flux increased linearly with increasing oxygen partial pressure gradient \( \ln(P_h/P_l) \). This finding indicates that the oxygen permeation through the BaCo0.4Fe0.4Zn0.2O3 disk membrane studied is controlled by the bulk diffusion of the oxygen ions.

The oxygen permeation flux of the BaCo0.4Fe0.4Zn0.2O3 disk membrane as a function of time at 900 °C is shown in Fig. 7. At the beginning, the oxygen permeation flux decreased slightly, but then it increases slowly with time. An oxygen permeation flux of about 0.40 ml/min/cm² was obtained at 900 °C and no decrease of the oxygen permeation flux was found during the permeation experiment. The possible reason for the steady permeation of BaCo0.4Fe0.4Zn0.2O3 is the doping of the B-site of the perovskite structure by a divalent redox-stable metal like zinc with a constant oxidation state of +2. This doping can avoid the reduction of the Co³⁺/Fe³⁺ ions to Co²⁺/Fe²⁺. We would like to point out that we have already performed the partial oxidation of methane to synthesis gas using the dense BaCo0.4Fe0.4Zn0.2O3 disk membrane reactor successfully, giving a methane conversion of about 95% and a CO selectivity higher than 93%. The membrane reactor has been continuously
operated for around 100 h without failure, which demonstrates that the BaCo$_0.4$Fe$_{0.4}$Zn$_{0.2}$O$_{3-δ}$ has promising application as a membrane reactor material. Detailed investigation of the POM reaction in a BaCo$_0.4$Fe$_{0.4}$Zn$_{0.2}$O$_{3-δ}$ membrane reactor will be reported later.

4. Conclusion

A novel zinc-doped mixed oxygen ion and electronic conducting membrane material based on BaCo$_0.4$Fe$_{0.4}$Zn$_{0.2}$O$_{3-δ}$ with pure perovskite structure was synthesized via a method of combining citric acid and EDTA complexation. The multi-run O$_2$-TPD profiles show an excellent structural reversibility. The introduction of small amounts of Zn on the B-site and the complete substitution of strontium by barium on the A-site can diminish the reduction of cobalt and iron, which stabilizes the structure. An oxygen permeation flux of 0.65 ml/min cm$^2$ was found at 950$^\circ$C and the membrane was steadily operated for more than 100 h in the oxygen permeation.

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