

## A Novel Zirconium-Based Perovskite-Type Membrane Material for Oxygen Permeation

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**Abstract:** A novel zirconium-based membrane material of  $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$  with cubic perovskite structure was synthesized for the first time through a method of citric and EDTA acid combined complexes. The structural stability was characterized by XRD,  $\text{O}_2$ -TPD and  $\text{H}_2$ -TPR techniques respectively. The high oxygen permeation flux of  $0.873 \text{ mL/cm}^2 \text{ min}$  at  $950^\circ\text{C}$  was obtained under He/Air gradient. Meanwhile, the single activation energy for oxygen permeation and the long-term steady operation of 200 h at  $800^\circ\text{C}$  were achieved.

**Keywords:** Perovskite, mixed-conducting, oxygen separation, zirconium.

Zirconia with fluorite structure stabilized by doping rare earth or alkaline earth metal oxides such as  $\text{Y}_2\text{O}_3$  and  $\text{CaO}$  (YSZ and CSZ) is a class of traditional mixed conducting membrane materials, which have been widely investigated for their high oxygen ionic conductivity and excellent chemical and thermal stability<sup>1-3</sup>. But the electronic conductivity of these materials is very small, unless operated with an internal or external circuitry, the oxygen flux through membranes in usual ranges of temperature and oxygen pressure is negligibly low, preventing their practical use as oxygen separation membrane materials. In order to improve the electronic conductivity, and thus to increase the oxygen permeation flux, the multivalent metal oxides such as  $\text{TiO}_2$  and  $\text{Tb}_2\text{O}_{3.5}$  were mixed into the lattice of YSZ and CSZ<sup>4</sup>. Unfortunately, the total conductivity was not enough for the use of oxygen extraction because of the limitation of solid solubility range of these multivalent oxides. To avoid this dilemma, dual phase composite membranes made from an oxygen-ion conducting oxide and an electron conducting noble metal have been investigated. However, in order to generate continuous pathways for ionic and electronic conduction, not only the amount of the noble metals is large, but also the techniques of fabrication are very complicated. In addition to the continuous pathways, at least one of the consistent materials should exhibit a large catalytic activity towards oxygen exchange. The shortcoming mentioned above will impair the application of dual phase membranes<sup>5</sup>.

Presently, it is reported that the perovskite-type materials  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  possess the highest oxygen permeation flux. And  $\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  and  $\text{La}_{0.2}\text{Ba}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  are two typical perovskite-type oxides

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that have been applied extensively in oxygen separation and selective oxidation of methane to ethene or syngas<sup>6-8</sup>. But all these membrane materials developed up to now could not supply the properties needed by practical use. The severe environments such as the large oxygen pressure gradient, the reducing atmosphere of monoxide or hydrogen, and the high dioxide concentration must be considered when applying the membranes into oxygen separation or continuous supplying oxygen for selective oxidation of light hydrocarbon. In order to improve these properties, a novel zirconium-based membrane material of  $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$  with cubic perovskite structure was synthesized and investigated.

### Experimental

The powders of the  $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$  were synthesized through a method of combined citric and EDTA acid complexes<sup>9</sup>. Membrane disks were obtained by pressing powders in a stainless die to pressures of 16-20 MPa. Green disk compacts were sintered in air at 1180°C for 10 h, with heating and cooling rate of 1-2°C /min. The density of the sintered disks was close to theoretical values. The system and experimental process of measurement of oxygen permeability was described in detail elsewhere<sup>9</sup>. The O<sub>2</sub>-TPD and H<sub>2</sub>-TPR experiments were performed on a homemade multi-function system<sup>10</sup>. The crystal structure was determined by XRD (Rigaku D-Max/RB).

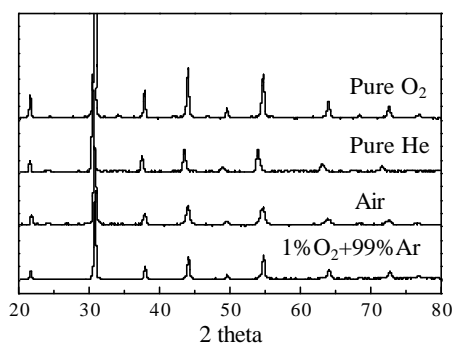
### Results and Discussion

**Figure 1** displayed the XRD patterns of the as-synthesized dense membrane material after treatment at 800°C under various oxygen partial pressures for 100 hours. The samples were obtained by the quenching method. During the entire oxygen activities investigated (1-10<sup>-5</sup> atm), the material showed the structure of cubic perovskite, and no phase transition was observed, demonstrating that the structure of the membrane disk was stable at 800°C under atmospheres with different oxygen activities. The high structural stability makes this as-synthesized membrane disk more suitable for constructing reactors for the oxygen separation and the partial oxidation of methane to syngas.

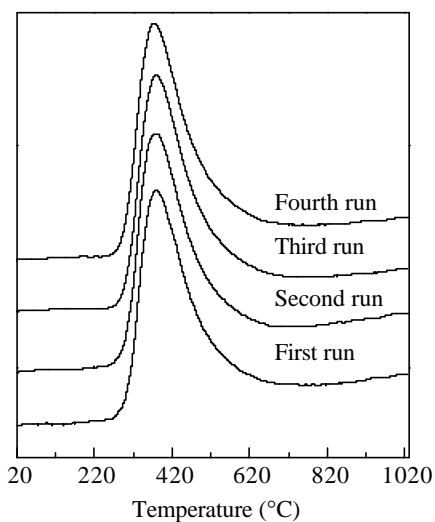
The structural stability of the  $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$  could also be demonstrated by the multi-run O<sub>2</sub>-TPD and the multi-run H<sub>2</sub>-TPR profiles. **Figure 2** showed the multi-run O<sub>2</sub>-TPD profiles, which revealed that the position and shape of peaks of four runs were completely uniform. This proved that the material possessed good oxygen adsorption and desorption ability, contributing the stable operation under He/air gradient. The multi-run H<sub>2</sub>-TPR profiles gave a prediction of the stability of this material under the reducing atmosphere and reaction conditions. **Figure 3** showed the multi-run H<sub>2</sub>-TPR profiles after recovering in 1 vol% O<sub>2</sub> and 99 vol% Ar gas mixture at 800°C for different time. The results indicated that the shape and position of the peaks were identical for all the recovering conditions. The shortest recovering time of 0.5 h was enough for restoring the structure of this material. The XRD patterns shown in **Figure 1** also

proved that the cubic perovskite structure was recovered completely. The best reversible structural stability of the  $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$  was evidenced.

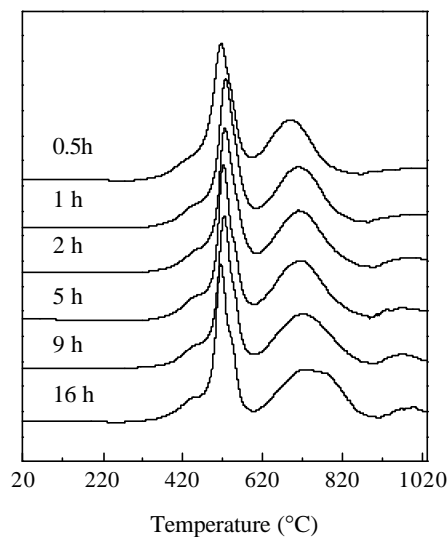
**Figure 1** XRD patterns of the  $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$  after treatment in atmospheres of different oxygen activities



**Figure 2** Multi-run  $\text{O}_2$ -TPD profiles of  $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$



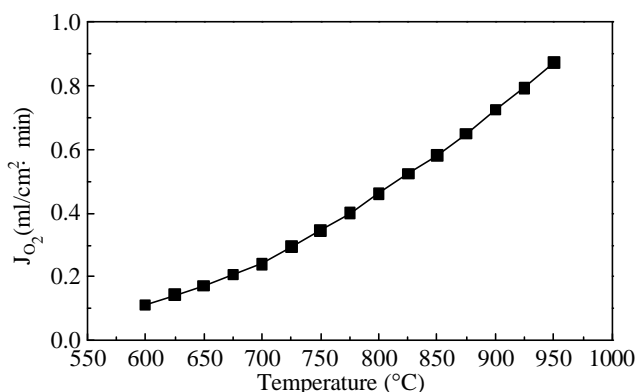
**Figure 3** Multi-run  $\text{H}_2$ -TPR profiles of  $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$



**Figure 4** showed the oxygen permeation fluxes under Air/He gradient, from which we could see that the oxygen permeation flux was elevated with the increase of the temperatures in the ranges of 600-950°C. The high oxygen permeation flux of  $0.90 \text{ ml/cm}^2 \cdot \text{min}$  was obtained at 950°C. Calculating the activation energy for oxygen permeation under the Air/He gave us an interesting result that only one activation energy was achieved in the temperature range of 600-950°C, which was very different from other materials. The single activation energy for oxygen permeation was accompanied

with the single peak of O<sub>2</sub>-TPD result and the stable cubic perovskite structure under various oxygen partial pressures.

**Figure 4** Oxygen permeation flux of BaCo<sub>0.4</sub>Fe<sub>0.4</sub>Zr<sub>0.2</sub>O<sub>3-δ</sub> under Air/He gradient



The long-term steady operation under air/He gradient was displayed in **Figure 5**. We could easily find that the oxygen permeation flux was unchanged during the whole 200 h. There was an important point that the operational temperature of our experiment was 800°C, not the usual operational temperature higher than 850°C. This showed that the novel zirconium-based materials could steadily operate under relatively lower temperature.

### Acknowledgments

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