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Novel cobalt-free tantalum-doped perovskite $BaFe_{1-y}Ta_yO_{3-\delta}$ with high oxygen permeation☆

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Cobalt-free perovskite-type oxides $BaFe_{1-y}Ta_yO_{3-\delta}$ ($0 \le y \le 0.2$) were synthesized *via* a simple solid state reaction. The cubic perovskite structure can be obtained when y is over 0.1. $BaFe_{0.9}Ta_{0.1}O_{3-\delta}$ (BFT0.1) membrane shows the highest oxygen permeation flux, which can reach 1.6 $ml\cdot min^{-1}\cdot cm^{-2}$ at 950 °C under the gradient of air/He. The O_2-TPD results reveal that $BaFe_{0.9}Ta_{0.1}O_{3-\delta}$ material shows an excellent reversibility and phase structure stability in air. The oxygen permeation flux is limited by the bulk diffusion when the membrane thickness is over 0.8 mm, and it is limited by both the bulk diffusion and the surface exchange when the membrane thickness is below 0.5 mm. Stable oxygen permeation fluxes are obtained during 180 h operation.

1. Introduction

Since Teraoka first reported that the $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ membrane has the stable oxygen permeation at elevated temperatures with infinite selectivity [1], mixed ionic-electronic conductor membranes (MIECs) have attracted much attention because of their wide and potential applications in catalytic membrane reactors [2–12], solid oxide fuel cells (SOFCs) [13–15], and gas sensors [16,17]. To acquire the high oxygen permeability for industrial demand, most of the membrane materials always contain cobalt, which is beneficial to activate oxygen molecules and deliver high oxygen permeation flux. However, cobalt can be easily reduced and evaporated, which leads to the poor stability of cobalt-containing membranes at high temperatures or the reducing atmosphere. Meanwhile, it is undesirable for practical application due to the high cost of Co. Therefore, developing new membrane materials with high oxygen permeability, good stability and low cost are required.

At present, $BaFeO_{3-\delta}$ membranes have received increasing attentions due to its low cost and high concentration of oxygen vacancy. However, the ionic radius of Ba^{2+} is too large to stabilize the perovskite structure. Most researchers have found that replacing A-site or B-site partly through doping can not just stabilize the perovskite structure [18–27], but also improve the oxygen permeability. Kida *et al.* [18] investigated that the oxygen permeation varies with the partially substitution of A-site by Na, Rb, Ca, Y and La. They found that the partial substitution of Ba by La, Y, Ca can successfully stabilize the cubic peroviskite structure. Specially, $Ba_{0.95}La_{0.05}FeO_{3-\delta}$ showed the highest oxygen permeability, which can reach 2.95 $ml\cdot min^{-1}\cdot cm^{-2}$ at 930 °C [24]. Zhu *et al.* [20,21] partially substitute Fe with Ce on the B-site and found that $BaCe_{0.15}Fe_{0.85}O_{3-\delta}$ membrane exhibits the highest oxygen permeation, which can reach 0.52 $ml\cdot min^{-1}\cdot cm^{-2}$ at 950 °C. Watanabe *et al.* [19] also reported that the $BaFe_{0.975}Zr_{0.025}O_{3-\delta}$ membrane has 1.3 $ml\cdot min^{-1}\cdot cm^{-2}$ oxygen permeation flux at 930 °C under an air/He gradient by doping Zr on the B-site.

Recently, Ta is reported to improve the structure stability of MIECs membrane by some groups [28–33]. Our group firstly developed a Ta doping perovskite membrane material, namely $BaCo_{0.7}Fe_{0.2}Ta_{0.1}O_{3-\delta}$, which presents outstanding phase structural stability and oxygen permeability [31–33]. After then, Chen *et al.* [28] found that the phase structure stability of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ membrane could be improved by doping Ta . Lohne [29] and Liu *et al.* [30] indicate the Ta can improve the stability of membrane in the reducing atmosphere at high temperature. In this work, we will systematically explore the influence of the partial substitution of Fe by Ta based on $BaFeO_{3-\delta}$. On basis of the definition of Goldschmidt tolerance factor (t) [34], the ideal cubic perovskite structure can be obtained only t close to 1. For $BaFeO_{3-\delta}$, the t is calculated to be 1.07 (Ba^{2+}: 0.161 nm, Fe^{3+}: 0.05975 nm, O^{2-}: 0.140 nm) [35,36], which is slightly larger than 1.0 (the optimum value). It is necessary to introduce a cation with a radius that is larger than that of Fe^{3+} or Fe^{4+} (B site), and simultaneously smaller than

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Ba^{2+} to stabilize the structure. The ion radius of Ta^{5+} is 0.064 nm, which is larger than Fe^{3+}/Fe^{4+} yet smaller than Ba^{2+}. Therefore, Ta is possibly the good candidate to dope $BaFeO_3$ and enhance its stability. In this paper, the $BaFe_{1-y}Ta_yO_{3-\delta}$ ($0 \le y \le 0.2$) samples were synthesized by a solid state reaction method. The oxygen permeability, phase structure, the rate-determining step for the oxygen transport and the operation stability will be studied in detail.

2. Experimental

Solid state reaction method was used to synthesize $BaFe_{1-y}Ta_yO_{3-\delta}$ ($0 \le y \le 0.2$) samples. According to the stoichiometry, $BaCO_3$, Ta_2O_5, and Fe_2O_3 (A.R. purity) were weighted, and hand-milled for 3 h in an agate mortar, and then ball-milled for 24 h in ethanol. After being calcined at 950 °C for 10 h, the powder were uniaxially pressed at 20 MPa in a stainless steel module to obtain the green disk membranes. The obtained disk membranes were calcined between 1175 °C and 1300 °C for 10 h. Only the sintered disk membranes with a relative density over 95%, which were tested by the Archimedes method in ethanol, could be used for oxygen permeation testing.

The crystal structures of $BaFe_{1-y}Ta_yO_{3-\delta}$ samples were analyzed by X-ray diffraction (XRD, Bruker-D8 ADVANCE). Scanning electron microscopy (SEM, Quanta 400) was used for analyzing the microstructure of membrane. O_2-TPD (Oxygen temperature-programmed desorption) was operated on a Micromeritics AutoChem 2920TM in our previous work [31].

$BaFe_{1-y}Ta_yO_{3-\delta}$ membranes were measured in homemade high-temperature apparatus, as reported in our previous work [31–33]. The $BaFe_{1-y}Ta_yO_{3-\delta}$ membrane polished using SiC paper was sealed by a ceramic sealant (Huitian, China). Air was supplied as the feed gas, and helium was supplied as the sweep gas, respectively. The effluents were analyzed by gas chromatography (GC, Agilent Technologies, 7890A). The soap bubble flow meter was used to measure the flow rates of the effluents. Due to the imperfect sealing, a little nitrogen can be detected, which was subtracted when calculating the membrane permeability. The particular calculation of the oxygen permeation flux was calculated as follows:

$$J_{O_2} = \left(C_{O_2} - \frac{C_{N_2}}{4.02}\right)\frac{F}{S} \qquad (1)$$

where C_{O_2} and C_{N_2} are the concentration of O_2 and N_2, respectively, which is calculated from GC calibration. S is the effective membrane area, and F is the total flow rate of the effluents.

3. Results and Discussion

Room-temperature XRD patterns of $BaFe_{1-y}Ta_yO_{3-\delta}$ membranes after sintering are shown in Fig. 1. As can be seen, $BaFeO_{3-\delta}$ membrane exhibits a hexagonal phase structure. After doping Ta, $BaFe_{1-y}Ta_yO_{3-\delta}$ membranes begin to change into the cubic perovskite phase. When $y \ge 0.1$, $BaFe_{1-y}Ta_yO_{3-\delta}$ membranes show pure cubic perovskite phase. According to the tolerance factor t defined by:

$$t = \frac{\gamma_A + \gamma_O}{\sqrt{2}(\gamma_B + \gamma_O)} \qquad (2)$$

where r_A (A-site ionic radii); r_B (B-site ionic radii); r_O (oxygen ionic radii). In the case of $0.75 \le t \le 1.0$, the cubic structure can be stabilized. For $BaFeO_{3-\delta}$, the t is estimated to be 1.07. (Ba^{2+}: 0.161 nm; Fe^{3+}: 0.05975 nm; O^{2-}: 0.140 nm) [35,36]. So as to obtain the cubic perovskite structure, Ta^{5+} (0.064 nm) is a good choice, since its ionic radius is between Fe^{3+} or Fe^{4+} (B site) and that of Ba^{2+} (A site). Fig. 2 shows the calculated t of different Ta doping. With an increasing of doping Ta^{5+}, the tolerance factor is a slight decrease and close to 1.0, which has an obvious influence on the phase structure of membrane, as shown in Fig. 1. Therefore, for obtaining the cubic perovskite phase, the concentration of doping Ta should be more than 0.1. Fig. 3 shows the XRD patterns of $BaFe_{0.9}Ta_{0.1}O_{3-\delta}$, $BaFe_{0.85}Ta_{0.15}O_{3-\delta}$

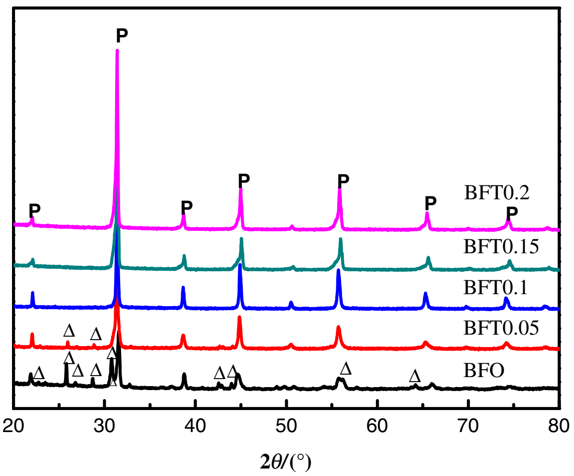

Fig. 1. The room-temperature XRD patterns of $BaFe_{1-y}Ta_yO_{3-\delta}$ membranes after sintering. (P-cubic perovskite phase; Δ-hexagonal structure phase).

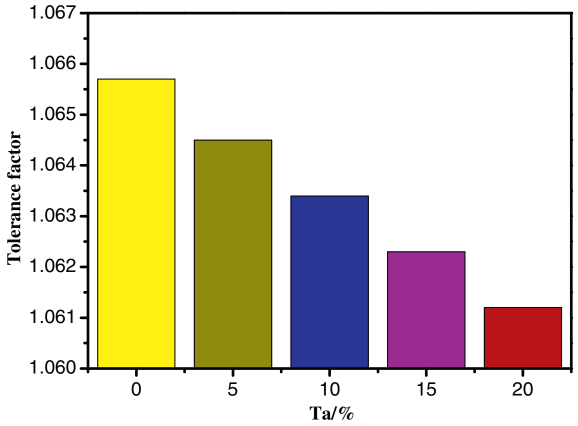

Fig. 2. Calculated tolerance factor (t) of different Ta dopings.

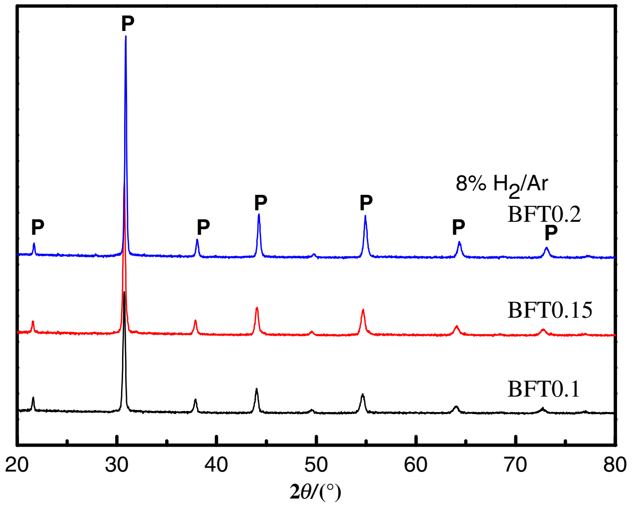

Fig. 3. XRD patterns of $BaFe_{1-y}Ta_yO_{3-\delta}$ ($y \ge 0.1$) samples after exposure to 8% H_2-Ar for 5 h at 900 °C.