Zirconium and Yttrium Co-Doped BaCo$_{0.8}$Zr$_{0.1}$Y$_{0.1}$O$_{3-\delta}$: A New Mixed-Conducting Perovskite Oxide-Based Membrane for Efficient and Stable Oxygen Permeation

Zixiang Xu, Jian Yu * and Wei Wang *

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 210009, China
* Correspondence: yuj@njtech.edu.cn (J.Y.); wangwei@njtech.edu.cn (W.W.)

Abstract: Oxygen permeation membranes (OPMs) are regarded as promising technology for pure oxygen production. Among various materials for OPMs, perovskite oxides with mixed electron and oxygen-ion (e$^-$/O$^{2-}$) conducting capability have attracted particular interest because of the high O$^{2-}$ conductivity and structural/compositional flexibility. However, BaCoO$_{3-\delta}$-based perovskites as one of the most investigated OPMs suffer from low oxygen permeation rate and inferior structural stability in CO$_2$-containing atmospheres. Herein, zirconium and yttrium co-doped BaCoO$_{3-\delta}$ (BaCo$_{1-x}$Zr$_x$Y$_x$O$_{3-\delta}$, x = 0, 0.05, 0.1 and 0.15) are designed and developed for efficient and stable OPMs by stabilizing the crystal structure of BaCoO$_{3-\delta}$. With the increased Zr/Y co-doping content, the crystal structural stability of doped BaCoO$_{3-\delta}$ is much improved although the oxygen permeation flux is slightly reduced. After optimizing the co-doping amount, BaCo$_{0.8}$Zr$_{0.1}$Y$_{0.1}$O$_{3-\delta}$ displays both a high rate and superior durability for oxygen permeation due to the well-balanced grain size, oxygen-ion mobility, crystal structural stability, oxygen vacancy concentration and surface exchange/bulk diffusion capability. Consequently, the BaCo$_{0.8}$Zr$_{0.1}$Y$_{0.1}$O$_{3-\delta}$ membrane delivers a high oxygen permeation rate of 1.3 mL min$^{-1}$ cm$^{-2}$ and relatively stable operation at 800 °C for 100 h. This work presents a promising co-doping strategy to boost the performance of perovskite-based OPMs, which can promote the industrial application of OPM technology.

Keywords: oxygen permeation; perovskite oxides; co-doping; structural stability; BaCoO$_{3-\delta}$

1. Introduction

Perovskite oxides with electron and oxygen-ion (e$^-$/O$^{2-}$) conducting capability have been extensively investigated in oxygen permeation membranes (OPMs), electrodes for ceramic fuel cells, catalysts for photo(electro)chemical water splitting and advanced oxidation processes due to the compositional/structural flexibility, tunable physical/chemical properties and high chemical/thermal stability [1–12]. Oxygen separation by using perovskite oxide-based membranes exhibited several advantages such as high selectivity and low cost over traditional pressure swing adsorption and low-temperature air separation [13–15]. Although numerous perovskite materials have been designed and developed as OPMs, the oxygen permeability and durability are still insufficient for practical applications. In addition, perovskite-based membranes should display superior structural and chemical stability under oxygen permeation conditions including high temperature, CO$_2$-containing atmosphere and large differences in oxygen partial pressures at two sides of OPMs [16–18]. However, the materials developed at present cannot fulfill the complex prerequisites of the large-scale oxygen permeation application. Thus, it is still of great significance to design new materials for efficient and stable oxygen permeation.

In past decades, perovskite oxides have received increasing interest as high-performance OPM materials due to the abundant compositional elements and easy adjustment in the
structure and chemical/physical properties [19,20]. Among them, cobalt (Co)-based perovskite membranes have attracted particular attention because of the superb oxygen permeation rate [21–25]. For instance, Teraoka et al. have firstly investigated the performance of La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-δ}$ OPMs and they found that Sr$_{0.8}$Co$_{0.2}$O$_{3-δ}$ (SCF) displayed a superior oxygen permeation rate to other investigated OPMs due to the larger oxygen vacancy concentration [26]. Nevertheless, SCF suffered from a serious crystal structure transition from cubic to brownmillerite under lower oxygen partial pressures and reduced temperatures (<800 °C), leading to a much-decreased oxygen permeability and durability [27]. To stabilize the crystal structure of SCF under oxygen permeation conditions, selectively doping at the A-site (e.g., Ba$^{2+}$, La$^{3+}$) and/or B-site (e.g., Nb$^{5+}$, Ti$^{4+}$) of SCF are reported to be effective to improve the crystal structure stability and/or oxygen permeation performance of SCF [28–31]. Caro et al. also studied the influences of Co/Fe ratios on the oxygen permeability of Pr-doped SCF for OPMs and Pr$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ perovskite showed a durable phase structure and a relatively high oxygen flux among various Pr-doped SCF perovskites [32]. In another study, Jin et al. have studied the effects of Zr$^{4+}$ doping amounts on the oxygen permeation performance and phase stability of SCF and the Zr$^{4+}$ doping greatly improved the stability of SCF for OPMs [33].

BaCo$_{3-δ}$ has been widely employed as a parent oxide for the design of numerous perovskite oxides for OPMs, showing relatively high oxygen permeability due to the superior oxygen surface exchange capability, large oxygen vacancy amount and free lattice volume, etc. [34,35]. However, an ideal perovskite structure cannot be formed in pure BaCo$_{3-δ}$ because of the large differences in the ionic sizes of Ba$^{2+}$ and Co$^{3+}$, leading to a highly distorted structure, which may block the bulk diffusion of O$^2-$ and electron transfer [36]. The doping strategy has been widely employed to design and develop BaCo$_{3-δ}$-based perovskite oxides for OPMs with improved oxygen permeation rate and durability by tuning the phase structure, oxygen vacancy amount, phase stability, oxygen mobility, oxygen surface exchange properties, etc. [37,38]. As one of the typically doped perovskite oxides for OPMs, Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ exhibited a cubic structure and a superior oxygen permeation rate [39]. Herein, two stable cations with relatively low valences (e.g., Zr$^{4+}$, Y$^{3+}$) are co-doped into the B-site of BaCo$_{3-δ}$ to enhance the oxygen permeation rate/durability and stabilize the phase structure. Y dopant is chosen to improve the structural stability of the perovskite-based OPMs, which also acts as a sintering aid to promote the densification of the membranes while Zr is selected to further improve the phase stability and the CO$_2$ resistance of the perovskite-based OPMs [40,41]. With the increased Zr/Y co-doping concentrations in BaCo$_{0.7}$Zr$_x$Y$_x$O$_{3-δ}$ (BCZY, x = 0, 0.05, 0.1 and 0.15), the phase transition from hexagonal (x = 0, BC) to cubic (x = 0.05, 0.1 and 0.15) was observed. The optimized BaCo$_{0.8}$Zr$_{0.1}$Y$_{0.1}$O$_{3-δ}$ perovskite displayed a relatively high rate and durability for oxygen permeation due to the well-balanced particle sizes, O$^2-$ conductivity, crystal structural stability, oxygen vacancy amount as well as bulk diffusion and surface exchange capability of oxygen species. As a result, the BaCo$_{0.8}$Zr$_{0.1}$Y$_{0.1}$O$_{3-δ}$ membrane displayed a superior oxygen permeation rate of 1.3 mL min$^{-1}$ cm$^{-2}$ and a relatively high oxygen permeation stability for 100 h at 800 °C. This study presents a highly promising mixed-conducting perovskite material for efficient and durable OPMs, promoting the industrialization of this technology.

2. Materials and Methods

2.1. Materials and Membrane Synthesis

Various BaCo$_{1-x}$Zr$_x$Y$_x$O$_{3-δ}$ (BCZY, x = 0, 0.05, 0.1 and 0.15) powders including BaCo$_{0.9}$Zr$_{0.05}$O$_{3-δ}$ (BCZY1), BaCo$_{0.8}$Zr$_{0.1}$Y$_{0.1}$O$_{3-δ}$ (BCZY2) and BaCo$_{0.7}$Zr$_{0.15}$Y$_{0.15}$O$_{3-δ}$ (BCZY3) were synthesized by a sol-gel route [42]. The obtained BCZY powders were then mixed in ethanol media by ball milling (Fritsch, Pulverisett 6) for 30 min to obtain fine and homogeneous powders. Dense BCZY membranes (15 mm in diameter) were fabricated by dry-pressing and further annealed at 1100 °C in air for 10 h [43]. The as-synthesized OPMs were further polished by 1500-mesh SiC sandpaper on
both sides to achieve various thicknesses of 0.6, 0.8 and 1.0 mm, which were then sealed on
the Al$_2$O$_3$ tube using Ag paste as the sealant. The oxygen permeation fluxes of OPMs were
obtained by analyzing the exhaust gas of the OPM-based reactor using gas chromatography.
The OPM-based reactor was slowly heated from room temperature (RT) to 900 °C with a
rate of 5 °C min$^{-1}$. Argon was used as the sweeping gas at a rate of 50 mL min$^{-1}$. The
oxygen permeation test was conducted at 900–600 °C with an interval of 50 °C.

2.2. Characterizations

The phase structures of various BCZY samples were acquired by X-ray diffraction
(XRD, Rigaku Smart Lab) at the 2θ range of 10–90°. The thermal expansion coefficients
(TECs) of the samples were acquired by a dilatometer (DIL 402C, Netzsch, Bayern, Germany)
at 300–900 °C in air. The cross-sectional and surface microstructures of BCZY
membranes were investigated by scanning electron microscopy (SEM, S-4800, Hitachi,
Tokyo, Japan). The thermal properties of various samples in the air were investigated by
thermogravimetric analysis (TGA, STA 449 F3, Netzsch, Bayern, Germany). The oxygen
non-stoichiometry ($\delta$, oxygen vacancy) values of various perovskite oxides at RT and high
temperatures were obtained by titration and TGA, respectively [44]. A mass spectrome-
ter (MS,HPR-20, Hiden Analytical, Warrington, England) was employed to measure the
oxygen desorption capability of the samples. The valence states of the samples at RT
were acquired by X-ray photoelectron spectroscopy (XPS, AXIS Supra, Shimadzu, Kyoto,
Japan). The electrical conductivities of various samples were obtained by a source meter
(Keithley 2420, Keithley, Cleveland, OH, America) at 800–500 °C with an interval of 25 °C.
The chemical diffusion coefficients ($D_{\text{chem}}$) and surface exchange coefficients ($K_{\text{chem}}$)
of various samples were obtained by electrical conductivity relaxation (ECR) curves tested at
700–500 °C. The ECR responses of various materials were obtained by suddenly switching
the oxygen partial pressure from 0.21 to 0.1 atm.

3. Results and Discussion

3.1. Basic Properties

Based on the RT-XRD patterns of various BCZY samples as depicted in Figure 1a,
BaCo$_{3-\delta}$ exhibited a hexagonal phase structure while the Zr and Y co-doped BCZY1,
BCZY2 and BCZY3 samples showed a pure cubic perovskite structure, indicating that Zr
and Y cations were successfully doped into the perovskite lattice without any impurities.
Based on the magnified XRD pattern, it was found that the increased co-doping amount
led to a shift in diffraction peaks to a smaller angle due to the large cation radius of Zr$^{4+}$
(0.72 Å) and Y$^{3+}$ (0.90 Å) than those of Co$^{x+}$ (0.745, 0.610 and 0.530 Å for Co$^{2+}$, Co$^{3+}$
and Co$^{4+}$). The thermodynamic stability of the cubic structure of BCZY1, BCZY2 and BCZY3
samples were further studied by high-temperature XRD (HT-XRD) with results shown in
Figure S1. It was found that BCZY1, BCZY2 and BCZY3 maintained a stable cubic phase
structure without any impurity phases at high temperatures, suggesting the high thermal
and phase structural stability of Zr and Y co-doped samples, which may be beneficial for
the high operation stability of OPMs. As depicted in Figure 1b, BCZY1, BCZY2 and BCZY3
displayed TEC values of 22.2, 20.8 and 18.2 × 10$^{-6}$ K$^{-1}$ at 300–900 °C. It has been reported
that the high TEC value of Co-rich perovskites was assigned to the thermal reduction in
Co$^{x+}$ cations at high temperatures, leading to a reduced amount of lattice oxygen and
increased lattice expansion [45]. The increase in the Zr/Y co-doping amount effectively
inhibited the thermal reduction in Co cations and gradually decreased the TEC value of
BaCo$_{3-\delta}$, benefiting the achievement of high operational stability of OPMs [46].
Based on the SEM images of various BCZY membranes as depicted in Figure 2 and Figure S2, clear grain boundaries and no interconnected pinholes were observed, indicating that the dense membranes were obtained. In addition, it was found that BCZY1, BCZY2, and BCZY3 membranes exhibited average grain sizes of 10–30, 3–5, and 1–2 μm, respectively. This indicates that the grain sizes of the as-synthesized perovskite membranes decreased significantly with increased Zr/Y co-doping amounts, which was consistent with Yao et al.’s work where the grain sizes of Zr-doped BaCo$_{0.7}$Fe$_{0.3}$O$_3$ decreased with increased Zr doping content [38]. The decrease in grain size of the membranes may be due to the inhibited crystal growth induced by the reduced amount of impurity phase existing at the grain boundary achieved by higher Zr/Y co-doping concentration [47].

Figure 2. Surface and cross-sectional SEM images of as-prepared BCZY membranes: (a,b) BCZY1, (c,d) BCZY2 and (e,f) BCZY3.

3.2. Oxygen Permeation Rates

Figure 3a shows the oxygen permeation fluxes of various BCZY membranes at different temperatures. As shown in Figure 3a, the oxygen permeation flux obviously increases with the increase in temperature, which is due to the increase in operating temperature is conducive to the bulk phase conduction and surface exchange of oxygen ions of perovskite materials, resulting in higher oxygen permeability [48]. The oxygen permeation rate of BaCo$_{3-\delta}$ at 900 °C was 2.9 mL min$^{-1}$ cm$^{-2}$, which was sharply reduced to only 1.2 mL min$^{-1}$ cm$^{-2}$ at 850 °C due to the detrimental phase transition. Nevertheless, after Zr and Y co-doping, the BCZY membranes displayed much superior oxygen permeability to those of BaCo$_{3-\delta}$ at lower temperatures. The oxygen permeation rates of BCZY1, BCZY2, BCZY3
and BaCoO$_{3-x}$ were 1.95, 1.28, 0.72 and 0.10 mL min$^{-1}$ cm$^{-2}$ at 800 °C. However, higher Zr/Y co-doping content reduced the oxygen permeation performance of BCZY membranes, which may be caused by the decreased oxygen vacancy concentration. To determine the main factor affecting oxygen permeation of BCZY membranes (e.g., surface exchange or bulk diffusion), the oxygen permeation rates of three BCZY membranes with different thicknesses of 1.0, 0.8 and 0.6 mm were tested at 900–600 °C as depicted in Figure 3b–d. It was found that reducing the thickness of the membrane greatly increased the oxygen permeability and the membrane thickness is nearly inversely proportional to the oxygen permeability (Figure S3). It suggests that the main rate-limiting step of oxygen permeation of BCZY membranes is O$^{2-}$ bulk diffusion and higher oxygen permeability can be achieved by further suppressing the thickness of the membranes [49].

**Figure 3.** (a) Oxygen permeation rates of BaCoO$_{3-x}$, BCZY1, BCZY2 and BCZY3 membranes with Ar as the sweeping gas at 600–900 °C; Oxygen permeation rates of (b) BCZY1, (c) BCZY2 and (d) BCZY3 membranes with different thicknesses.

### 3.3. Oxygen Vacancies, Oxidation States and Transport/Diffusion Capability

Figure 4a displays the TGA curves of various BCZY samples, demonstrating the weight losses of various co-doped perovskites in the air at 50–1000 °C. It was found that the weight loss of the three samples followed the sequence of BCZY1 > BCZY2 > BCZY3. As shown in Figure 4b, BCZY1 exhibited the largest oxygen vacancy concentration at 400–900 °C while the oxygen vacancy concentration of BCZY3 was much lower than those of the other two samples. It suggested that Zr/Y co-doping inhibited the generation of oxygen vacancies due to the higher valence states of these dopants. A large oxygen vacancy amount favors O$^{2-}$ conduction and improves the oxygen permeability, which may bring a negative effect on the operational stability of OPMs [50]. To further study the effects of Zr/Y co-doping contents on the O$^{2-}$ mobility of various BCZY samples, oxygen temperature programmed desorption (O$_2$-TPD) is employed with results shown in Figure 4c. It was found that the initial oxygen desorption temperature of BCZY1, BCZY2 and BCZY3 were 220, 290 and 310 °C, respectively. BCZY1 exhibited the lowest desorption temperature indicating its highest O$^{2-}$ mobility [51]. The Zr/Y co-doping of reduced the O$^{2-}$ mobility, which may contribute to the decreased oxygen permeation rate with increased co-doping amounts. XPS was further conducted to study the influences of Zr/Y co-doping on the oxidation states of B-site Co cations. Based on the Co 2p/Ba 3d XPS spectra and corresponding fitting results of various BCZY samples as depicted in Figure 4d–f and Table S1, the Co$^{4+}$ amounts of BCZY1, BCZY2 and BCZY3 were 33.0%, 49.3% and 57.9% based on the binding
energy positions of Co\(^{4+}\) and Co\(^{3+}\) at 781.0 ± 0.3 and 778.5 ± 0.3 eV in the XPS spectra [52]. The oxygen vacancy amounts of BCZY1, BCZY2 and BCZY3 at RT were calculated to be 0.327, 0.253 and 0.220 based on the XPS results, matching well with the results obtained by titration. These results indicated that the increase in the Zr/Y co-doping amount reduces the oxygen vacancy amount and then the oxygen permeability.

![Graphs](image)

**Figure 4.** (a) TGA curves; (b) oxygen vacancy concentration; (c) O\(_2\)-TPD curves of BCZY1, BCZY2 and BCZY3; Co 2p and Ba 3d XPS spectra of (d) BCZY1, (e) BCZY2 and (f) BCZY3.

The electrical conductivities of various BCZY samples were tested in air at 500–800 °C as depicted in Figure 5a. Since the ionic conductivity of perovskite oxides is much lower than the electronic conductivity, the electrical conductivity of BCZY samples can be considered electronic conductivity [53,54]. With the increase in the Zr/Y co-doping amount, the electronic conductivities of BCZY were remarkably reduced, especially for the BCZY3 sample. For instance, the electronic conductivities of BCZY1, BCZY2 and BCZY3 samples followed the sequence of BCZY1 > BCZY2 > BCZY3, indicating that the Zr/Y co-doping reduced both the surface exchange and bulk diffusion capability of oxygen species.

![Graphs](image)

**Figure 5.** (a) Electrical conductivities of BCZY1, BCZY2, BCZY3 in air; Arrhenius plots of (b) \(D_\text{chem}\) and (c) \(K_\text{chem}\) values of BCZY samples obtained by ECR.
3.4. Oxygen Permeation Stability, Structural Stability and CO$_2$ Tolerance

Besides the high oxygen permeability, operational stability is also crucial for the OPMs. In this work, the long-term stability of BCZY1, BCZY2 and BCZY3 membranes for oxygen permeation were tested at 800 °C. As depicted in Figure 6a, the oxygen permeation rate of BCZY1 was sharply suppressed from 2.02 to 1.47 mL min$^{-1}$ cm$^{-2}$ after 100 h’s test while BCZY2 and BCZY3 displayed more stable oxygen permeation rates for 100 h. It suggested the Zr/Y co-doping significantly improved the operational stability of the perovskite-based membranes. Furthermore, the phase structures of BCZY1, BCZY2 and BCZY3 membranes after 100 h’s operation were also investigated by XRD as shown in Figure 6b–d. It has been reported that a small amount of carbonate was formed on the surface of BaCoO$_{3-δ}$-based membranes such as BaCo$_{0.7}$Fe$_{0.2}$Sn$_{0.1}$O$_{3-δ}$, which was detrimental to achieving high operational stability of OPMs [56]. As depicted in Figure 6b–d, no obvious changes in the phase structures of BCZY2 and BCZY3 membranes on the air and Ar sides were observed and no carbonates were formed after 100 h’s oxygen permeation test. However, barium carbonate (BaCO$_3$) and BaCoO$_{3-δ}$ impurities were observed in the BCZY1 membrane after 100 h’s oxygen permeation, indicating inferior CO$_2$ tolerance and structural stability of BCZY1. It can be concluded that the Zr/Y co-doping at higher concentrations is crucial to enhance the CO$_2$ resistance of BaCoO$_{3-δ}$-based membranes.

![Figure 6](image-url)

**Figure 6.** (a) Oxygen permeation stability tests of 0.8 mm-thick BCZY1, BCZY2 and BCZY3 membranes at 800 °C; RT-XRD patterns of BCZY membranes after the 100 h’s oxygen permeation: (b) BCZY1, (c) BCZY2 and (d) BCZY3.

To further study the CO$_2$ tolerance of BCZY-based OPMs, oxygen permeation tests were performed at 800 °C under different sweeping gases in a sequence of pure Ar/5%CO$_2$ + Ar/pure Ar for 900 min. As displayed in Figure 7a, the oxygen permeability of all BCZY membranes was reduced when the sweeping gas was changed from Ar to 5%CO$_2$ + Ar, which was assigned to the decreased amount of active sites induced by the competitive CO$_2$ adsorption and/or the possible carbonate formation on the OPM surface [57,58]. Among them, the BCZY2 membrane delivered the highest oxygen permeation rate of 0.5 mL min$^{-1}$ cm$^{-2}$ after 300 min’s operation in the CO$_2$-Ar atmosphere, which was attributed to the improved CO$_2$ tolerance and suitable oxygen vacancy concentration [59]. When the sweeping gas was changed back to Ar, the permeation fluxes of BCZY1, BCZY2 and BCZY3 were 1.75, 1.2 and 0.7 mL min$^{-1}$ cm$^{-2}$, respectively. It should be noted that the oxygen permeation rates of BCZY2 and BCZY3 samples were mostly recovered to
the primary value due to the higher Zr/Y co-doping concentrations to improve the CO₂ tolerance of OPMs [60]. Furthermore, BCZY1, BCZY2 and BCZY3 powders were calcined in various atmospheres such as 5%CO₂ + Ar, air and O₂ at 800 °C for 20 h to investigate the influences of the treatment atmosphere on the structural stability of perovskite-based OPMs as shown in Figure 7b–d. As shown in Figure 7b, XRD peaks assigned to BaCO₃ were detected for all three samples after the treatment in 5%CO₂ + Ar while the increased Zr/Y co-doping amount led to much-reduced peak intensity of such BaCO₃ impurity, which was assigned to the increased metal-oxygen bonding in perovskite oxides [61]. In addition, the BaCoO₃δ minor phase was only detected in the BCZY1 sample after the calcination in the air atmosphere for 20 h while BaCoO₃δ minor phase was also observed in BCZY1 and BCZY2 samples after treatment in the O₂ atmosphere for 20 h (Figure 7c,d). Therefore, we can conclude that the Zr/Y co-doping at higher concentrations significantly improved the phase structural stability of BaCoO₃δ-based perovskites towards stable oxygen permeation.

![Figure 7.](image-url)

**Figure 7.** (a) Oxygen permeation rates of various BCZY membranes under Ar, CO₂-Ar and Ar atmospheres at 800 °C; RT-XRD patterns of BCZY1, BCZY2 and BCZY3 samples after a treatment in (b) 5%CO₂ + Ar, (c) air and (d) O₂ atmospheres for 20 h at 800 °C.

### 4. Conclusions

In summary, the influences of Zr/Y co-doping amounts on the phase structure, grain sizes, electronic conductivity, structural stability, surface exchange/bulk diffusion properties and oxygen permeability of BaCoO₃δ were investigated. With the increased Zr/Y co-doping amount, the electrical conductivity, oxygen vacancy amount and surface exchange/bulk diffusion coefficients of BCZY were gradually decreased and the phase structural stability of co-doped perovskites was improved, leading to gradually reduced oxygen permeability and enhanced oxygen permeation durability. BaCo₀.₈Zr₀.₁Y₀.₁O₃₋δ with optimized Zr/Y co-doping amount exhibited high permeability and durability for oxygen permeation due to the trade-off between various crucial factors to determine the oxygen permeation performance including grain sizes, crystal structural stability, oxygen vacancy amount and surface exchange/bulk diffusion capability. Thus, BaCo₀.₈Zr₀.₁Y₀.₁O₃₋δ-based OPMs showed a superb oxygen permeation rate of 1.3 mL min⁻¹ cm⁻² and a relatively durable operation for 100 h at 800 °C. This work can provide a high-performance perovskite material for OPMs, which may accelerate the industrialization of OPM technology for oxygen separation.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/membranes12090831/s1, Figure S1. HT-XRD patterns of BCZY powder at different temperatures: BCZY1 (a), BCZY2 (b) and BCZY3 (c); Figure S2. Surface SEM image of the BCZY1 membrane; Figure S3. Relationship between oxygen permeation fluxes and the reciprocal thickness of BCZY membranes at different temperatures: (a) BCZY1, (b) BCZY2 and (c) BCZY3; Figure S4. ECR response curves of BCZY obtained between 500 and 700 °C: (a) BCZY1, (b) BCZY2 and (c) BCZY3; Table S1. Average valence states of B-site cations and oxygen vacancy amount of various BCZY samples obtained by XPS and titration; Table S2. The values of $D_{\text{chem}}$ and $K_{\text{chem}}$ of BCZY samples at various temperatures.

Author Contributions: Conceptualization, W.W. and J.Y.; Formal analysis, Z.X.; Investigation, Z.X.; Writing-original draft, Z.X.; Visualization, Z.X.; Data curation, Z.X.; Supervision, W.W. and J.Y.; Writing-review & editing, W.W. and J.Y.; Validation, Z.X., J.Y. and W.W.; Funding acquisition, W.W. All authors have read and agreed to the published version of the manuscript.

Funding: This work is supported by National Natural Science Foundation of China (No. 21908106) and Jiangsu Natural Science Foundation (No. BK20190682).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Song, Y.; Chen, J.; Yang, M.; Xu, M.; Liu, D.; Liang, M.; Wang, Y.; Ran, R.; Wang, W.; Ciucci, F.; et al. Realizing simultaneous detrimental reactions suppression and multiple benefits generation from nickel doping towards improved protonic ceramic fuel cell performance. Small 2022, 18, 2200450. [CrossRef] [PubMed]

2. Xiong, X.; Yu, J.; Huang, X.; Zou, D.; Song, Y.; Xu, M.; Ran, R.; Wang, W.; Zhou, W.; Shao, Z. Slightly ruthenium doping enables better alloy nanoparticle exsolution of perovskite anode for high-performance direct-ammonia solid oxide fuel cells. J. Mater. Sci. Technol. 2022, 125, 51–58. [CrossRef]

3. Duan, C.; Kee, R.; Zhu, H.; Karakaya, C.; Chen, Y.; Ricote, S.; Jarry, A.; Crumlin, E.; Hook, D.; Braun, R.; et al. Highly durable, coking and sulfur tolerant, fuel-flexible protonic ceramic fuel cells. Nature 2018, 557, 217–222. [CrossRef]

4. Duan, C.; Kee, R.; Zhu, H.; Karakaya, C.; Chen, Y.; Ricote, S.; Jarry, A.; Crumlin, E.; Hook, D.; Braun, R.; et al. Highly durable, coking and sulfur tolerant, fuel-flexible protonic ceramic fuel cells. Nature 2018, 557, 217–222. [CrossRef] [PubMed]

5. Yang, G.; Su, C.; Shi, H.; Zhu, Y.; Song, Y.; Zhou, W.; Shao, Z. Toward reducing the operation temperature of solid oxide fuel cells: Our past 15 years of efforts in cathode development. Energy Fuels 2020, 34, 15169–15194. [CrossRef]

6. Han, N.; Zhang, W.; Guo, W.; Xie, S.; Zhang, C.; Zhang, X.; Fransaer, J.; Liu, S. Novel oxygen permeable hollow fiber perovskite membrane with surface wrinkles. Sep. Purif. Technol. 2021, 261, 118295. [CrossRef]

7. Buck, F.; Feldhoff, A.; Caro, J.; Schiestel, T. Permeation improvement of LCCF hollow fiber membranes by spinning and sintering optimization. Sep. Purif. Technol. 2021, 259, 118023. [CrossRef]

8. Escolástico, S.; Schulze-Kueppers, F.; Baumann, S.; Haas-Santo, K.; Dittmeyer, R. Development and proof of concept of a compact metallic reactor for MIEC ceramic membranes. Membranes 2021, 11, 541. [CrossRef]

9. Larrning, Y.; Vigen, C.; Ahouanto, F.; Fontaine, M.; Peters, T.; Smith, J.; Norby, T.; Brederen, R. Investigation of $La_{1-x}Sr_xCrO_3$-δ (x ~ 0.1) as membrane for hydrogen production. Membranes 2012, 2, 665–686. [CrossRef]

10. Han, X.; Liu, P.; Ran, R.; Wang, W.; Zhou, W.; Shao, Z. Non-metal fluorine doping in Ruddlesden-Popper perovskite oxide enables high-efficiency photocatalytic water splitting for hydrogen production. Mater. Today Energy 2022, 23, 100896. [CrossRef]

11. Xiao, H.; Liu, P.; Wang, W.; Ran, R.; Zhou, W.; Shao, Z. Enhancing the photocatalytic activity of Ruddlesden-Popper $Sr_2\text{TiO}_4$ for hydrogen evolution through synergistic silver doping and moderate reducing pretreatment. Mater. Today Energy 2022, 23, 100899. [CrossRef]

12. Yang, L.; Li, Y.; Sun, Y.; Wang, W.; Shao, Z. Perovskite oxides in catalytic combustion of volatile organic compounds: Recent advances and future prospects. Energy Environ. Mater. 2022, 5, 751–776. [CrossRef]

13. Chen, T.; Miao, J.; Zhu, M.; Ran, R.; Zhou, W.; Shao, Z. Thermal reduction-assisted electronic structure tuning of perovskite oxide as catalyst for efficient advanced oxidation. Compos. Part B-Eng. 2021, 207, 108577. [CrossRef]

14. Tarutina, L.; Vdovin, G.; Lyagaeva, J.; Medvedev, D. Comprehensive analysis of oxygen transport properties of a BaFe$_{0.7}$Zr$_{0.3}$O$_{3-\delta}$-based mixed ionic-electronic conductor. J. Membr. Sci. 2021, 624, 119125. [CrossRef]

15. Schulz, M.; Pippardt, U.; Kiesel, L.; Ritter, K.; Kriegl, R. Oxygen permeation of various archetypes of oxygen membranes based on BSCF. AIChE J. 2012, 58, 3195–3202. [CrossRef]

16. Damiani, D.; Litynski, J.; Mcllvried, H.; Vikara, D.; Srivastava, R. The US department of energy’s R&D program to reduce greenhouse gas emissions through beneficial uses of carbon dioxide. Greenh. Gases 2012, 2, 9–19.
16. Sunarso, J.; Hashim, S.; Zhu, N.; Zhou, W. Perovskite oxide applications in high temperature oxygen separation, solid oxide fuel cell and membrane reactor: A review. *Prog. Energy Combust. Sci.* 2017, 61, 57–77. [CrossRef]

17. Chen, G.; Zhao, Z.; Widenmeyer, M.; Yan, R.; Wang, L.; Feldhoff, A.; Weidenkaff, A. Synthesis and characterization of 40 wt% Ce0.9Eu0.1O2−δ−60 wt% Nd0.7−xSr1−xFe3O4−δ dual-phase membranes for efficient oxygen separation. *Membranes* 2020, 10, 183. [CrossRef]

18. Zhang, Z.; Ning, K.; Xu, Z.; Zheng, Q.; Tan, J.; Liu, Z.; Wu, Z.; Zhang, G.; Jin, W. Highly efficient preparation of Ce0.8Sm0.2O2−δ−SrCo0.8Nb0.2O3−δ dual-phase four-channel hollow fiber membrane via one-step thermal processing approach. *J. Membr. Sci.* 2021, 620, 118752. [CrossRef]

19. Zhang, K.; Liu, M.; Zhao, L.; Yan, J.; Wang, Z. Lead and tungsten double stabilizing cobalt-based perovskite oxygen permeation membranes for clean energy delivery. *Int. J. Energy Res.* 2020, 44, 6259–6268. [CrossRef]

20. Guironnet, L.; Geffroy, P.; Tessier-Doyen, N.; Boulle, A.; Richet, N.; Chartier, T. The surface roughness effect on electrochemical properties of La0.8Sr0.2O1.9−δ perovskite membranes for oxygen transport membranes. *J. Membr. Sci.* 2019, 588, 117199. [CrossRef]

21. Shao, Z.; Xiong, G.; Dong, H.; Yang, W.; Lin, L. Synthesis, oxygen permeation study and membrane performance of Ba0.5Sr0.5Co0.8Fe0.2O3−δ oxygen-permeable dense ceramic reactor for partial oxidation of methane to syngas. *Sep. Purif. Technol.* 2001, 25, 97–116. [CrossRef]

22. Duffy, J.; Meng, Y.; Abernathy, H.; Brinkman, K. Surface and bulk oxygen kinetics of BaCo0.4Fe0.4Zr0.2−xYxO3−δ triple conducting electrode membranes. *Membranes* 2021, 11, 766. [CrossRef]

23. Zhang, D.; Zhang, H.; Jiang, Y.; Ye, S.; Qiang, L.; Lin, B. A stable Zr-Y co-doped perovskite BaCo0.4Fe0.4Zr0.1Y0.1O3−δ ceramic membrane for highly efficient oxygen separation. *Sep. Purif. Technol.* 2022, 295, 121206. [CrossRef]

24. Schulze-Kueppers, F.; Baumann, S.; Meulenberg, W.A.; Stoever, D.; Buchkremer, H. Manufacturing and performance of advanced supported Ba0.5Sr0.5Co0.8Fe0.2O3−δ (BSCF) oxygen transport membranes. *J. Membr. Sci.* 2013, 433, 121–125. [CrossRef]

25. Kashyap, V.; Jaiswal, S.; Kumar, J. Effect of Zr4+ on the phase stability and oxygen permeation characteristics of SrCo0.8Fe0.2−δZr0.1O3−δ (y ≤ 0.1) membranes. *Ionics* 2020, 26, 1895–1911. [CrossRef]

26. Teraoka, Y.; Zhang, H.; Furukawa, S.; Yamazoe, N. Oxygen permeation through perovskite-type oxides. *Chem. Lett.* 1985, 11, 1743–1746. [CrossRef]

27. McIntosh, S.; Vente, J.; Haitie, W.; Blank, D.; Bouwmeester, H. Phase stability and oxygen non-stoichiometry of SrCo0.8Fe0.2O3−δ measured by in situ neutron diffraction. *Solid State Ion.* 2006, 177, 833–842. [CrossRef]

28. Han, N.; Zhang, C.; Tan, K.; Wang, Z.; Kawi, S.; Liu, S. Re-evaluation of La0.6Sr0.4Co0.2Fe0.8O3−δ hollow fiber membranes for oxygen separation after long-term storage of five and ten years. *J. Membr. Sci.* 2019, 587, 117180. [CrossRef]

29. McIntosh, S.; Vente, J.; Haitie, W.; Blank, D.; Bouwmeester, H. Structure and oxygen stoichiometry of SrCo0.8Fe0.2O3−δ and Ba0.5Sr0.5Co0.8Fe0.2O3−δ. *Solid State Ion.* 2006, 177, 1737–1742. [CrossRef]

30. Kawahara, A.; Takahashi, Y.; Hirano, Y.; Hirano, M.; Ishihara, T. High oxygen permeation rate in La0.6Sr0.4Ti0.3Fe0.7O3−δ thin membrane on a porous support with multichannel structure for CH4 partial oxidation. *Ind. Eng. Chem. Res.* 2010, 49, 5511–5516. [CrossRef]

31. Liu, C.; Cheng, H.; Yan, G.; Zhao, H.; Lu, X.; Wang, P. Effects of B-site Nb doping on the CO2 resistance and rate-controlling step of Ce0.8Gd0.2O2−δ−Pr0.6Sr0.4Co0.5Fe0.5O3−δ dual-phase membranes. *J. Membr. Sci.* 2018, 53, 11962–11976. [CrossRef]

32. Partovi, K.; Liang, F.; Ravkina, O.; Caro, J. High-flux oxygen-transporting membrane Pr0.6Sr0.4Co0.5Fe0.5O3−δ: CO2 stability and microstructure. *ACS Appl. Mater. Interfaces* 2014, 6, 10274–10282. [CrossRef] [PubMed]

33. Yang, L.; Tan, L.; Gu, X.; Jin, W.; Zhang, L.; Xu, N. A new series of Sr(Co, Fe, Zr)O3−δ perovskite-type membrane materials for oxygen permeation. *Ind. Eng. Chem. Res.* 2003, 42, 2299–2305. [CrossRef]

34. Song, S.; Zhang, P.; Han, M.; Singhal, S. Oxygen permeation and partial oxidation of methane reaction in Ba0.9Co0.7Fe0.2Nb0.1O3−δ oxygen permeation membrane. *J. Membr. Sci.* 2012, 415, 654–662. [CrossRef]

35. Yang, F.; Zhao, H.; Yang, J.; Fang, M.; Lu, Y.; Du, Z.; Swierczek, K.; Zheng, K. Structure and oxygen permeability of BaCo0.7Fe0.3−δIn0.5−δ ceramic membranes. *J. Membr. Sci.* 2015, 492, 559–567. [CrossRef]

36. Felser, C.; Yamaura, K.; Cava, R.J. The electronic structure of hexagonal BaCoO3. *J. Solid State Chem.* 1999, 146, 411–417. [CrossRef]

37. Cheng, H.; Yao, W.; Lu, X.; Zhou, Z.; Li, C.; Liu, J. Structural stability and oxygen permeability of BaCo0.7Fe0.3M0.1O3−δ (M = Ta, Nb, Zr) ceramic membranes for producing hydrogen from coke oven gas. *Fuel Process. Technol.* 2015, 131, 36–44. [CrossRef]

38. Yao, W.; Cheng, H.; Zhao, H.; Lu, X.; Zou, X.; Li, S.; Li, C. Synthesis, oxygen permeability, and structural stability of BaCo0.7Fe0.3−δZr0.1−δ ceramic membranes. *J. Membr. Sci.* 2016, 504, 251–262. [CrossRef]

39. Li, X.; Kerstiens, T.; Markus, T. Oxygen permeability and phase stability of Ba0.5Sr0.5Co0.8Fe0.2O3−δ perovskite at intermediate temperatures. *J. Membr. Sci.* 2013, 438, 83–89. [CrossRef]

40. Li, X.; Zhao, H.; Shen, W.; Gao, F.; Huang, X.; Li, Y.; Zhu, Z. Synthesis and properties of Y-doped SrTiO3 as an anode material for SOFCs. *J. Power Sources* 2007, 166, 47–52. [CrossRef]

41. Jeong, N.; Lee, J.; Tae, E.; Lee, Y.; Yoon, K. Acidity scale for metal oxides and Sanderson’s electronegativities of lanthanide elements. *Angew. Chem. Int. Ed.* 2008, 47, 10128–10132. [CrossRef] [PubMed]

42. Liu, C.L.; Chen, D.; Wang, W. Hydrogen-rich syngas production from chemical looping steam reforming of bio-oil model compound: Effect of bimetal on LaNi0.8M0.2O3 (M = Fe, Co, Cu, and Mn). *Int. J. Energy Res.* 2019, 43, 4534–4545. [CrossRef]
43. Zhang, J.; Zhang, Z.; Chen, Y.; Xu, X.; Zhou, C.; Yang, G.; Zhou, W.; Shan, Z. Materials design for ceramic oxygen permeation membranes: Single perovskite vs. single/double perovskite composite, a case study of tungsten-doped barium strontium cobalt ferrite. J. Membr. Sci. 2018, 566, 278–287. [CrossRef]

44. Kuai, X.; Yang, G.; Chen, Y.; Sun, H.; Dai, J.; Song, Y.; Ran, R.; Wang, W.; Zhou, W.; Shao, Z. Boosting the activity of BaCo0.4Fe0.6Zr0.1Y0.1O3–δ perovskite for oxygen reduction reactions at low-to-intermediate temperatures through tuning B-Site cation deficiency. Adv. Energy Mater. 2019, 9, 1902384. [CrossRef]

45. McIntosh, S.; Vente, J.; Haije, W.; Blank, D.; Bouwmeester, H. Oxygen stoichiometry and chemical expansion of BaFe1−xLa0.5Ca0.5FeO3−δ measured by in situ neutron diffraction. Chem. Mater. 2013, 25, 18, 2187–2193. [CrossRef]

46. Luo, H.; Tian, B.; Wei, Y.; Wang, H.; Jiang, H.; Caro, J. Oxygen permeability and structural stability of a novel tantalum-doped perovskite BaCo0.7Fe0.2Ta0.1O3–δ. AIChE J. 2010, 56, 604–610. [CrossRef]

47. Watanabe, K.; Takauchi, D.; Yuasa, M.; Kida, T.; Shimanoe, K.; Teraoka, Y.; Yamazoe, N. Oxygen permeation properties of Co-free perovskite-type oxide membranes based on BaFe1−yZr0.3O3–δ. J. Electrochem. Soc. 2009, 156, E81–E85. [CrossRef]

48. Hong, W.; Choi, G. Oxygen permeation of BSCF membrane with varying thickness and surface coating. J. Membr. Sci. 2010, 346, 353–360. [CrossRef]

49. Liao, Q.; Wang, Y.; Chen, Y.; Wei, Y.; Wang, H. Novel bifunctional tantalum and bismuth co-doped perovskite BaBi0.05Co0.8Ta0.15O3–δ with high oxygen permeation. J. Membr. Sci. 2014, 468, 184–191. [CrossRef]

50. Li, K.; Zhao, H.; Lu, Y.; Ma, Y.; Du, Z.; Zhang, Z. High CO2 tolerance oxygen permeation membranes BaFe0.95−xCa0.05Ti3xO3−δ. J. Membr. Sci. 2018, 550, 302–312. [CrossRef]

51. Song, Y.; Chen, Y.; Wang, W.; Zhou, C.; Zhong, Y.; Yang, G.; Zhou, W.; Liu, M.; Shao, Z. Self-assembled triple-conducting nanocomposite as a superior protonic ceramic fuel cell cathode. Joule 2019, 3, 2842–2853. [CrossRef]

52. Cui, X.; O’Hayre, R.; Pylypenko, S.; Zhang, L.; Zeng, L.; Zhang, X.; Hua, Z.; Chen, H.; Shi, J. Fabrication of a mesoporous Ba0.5Sr0.5Co0.8Fe0.2O3–δ perovskite as a low-cost and efficient catalyst for oxygen reduction. Dalton Trans. 2017, 46, 13903–13911. [CrossRef] [PubMed]

53. Zou, D.; Yi, Y.; Song, Y.; Guan, D.; Xu, M.; Ran, R.; Wang, W.; Zhou, W.; Shao, Z. The BaCe0.16Y0.04Fe0.6O3–δ nanocomposite: A new high-performance cobalt-free triple-conducting cathode for protonic ceramic fuel cells operating at reduced temperatures. J. Mater. Chem. A 2022, 10, 5381–5390. [CrossRef]

54. Liang, M.; He, F.; Zhou, C.; Chen, Y.; Ran, R.; Yang, G.; Zhou, W.; Shao, Z. Nickel-doped BaCo0.4Fe0.6Zr0.1Y0.1O3–δ as a new high-performance cathode for both oxygen-ion and proton conducting fuel cells. Chem. Eng. J. 2021, 420, 127717. [CrossRef]

55. Zhao, H.; Xu, N.; Cheng, Y.; Wei, W.; Chen, N.; Ding, W.; Lu, X.; Li, F. Investigation of mixed conductor BaCo0.7Fe0.3−xYxO3−δ with high oxygen permeability. J. Phys. Chem. C 2010, 114, 17975–17981. [CrossRef]

56. Zhang, Z.; Chen, Y.; Tade, M.; Hao, Y.; Liu, S.; Shao, Z. Tin-doped perovskite mixed conducting membrane for efficient air separation. J. Mater. Chem. A 2014, 2, 9666–9674. [CrossRef]

57. Czuprut, O.; Arnold, M.; Schirrmeister, S.; Schiestel, T.; Caro, J. Influence of CO2 on the oxygen permeation performance of perovskite-type BaCo0.4Fe0.6Zr0.1O3–δ hollow fiber membranes. J. Membr. Sci. 2010, 364, 132–137. [CrossRef]

58. Zhang, Z.; Chen, D.; Dong, F.; Shao, Z. Efficient and CO2-tolerant oxygen transport membranes prepared from high-valence B-site substituted cobalt-free SrFeO3–δ. J. Membr. Sci. 2015, 495, 187–197. [CrossRef]

59. Liu, J.; Cheng, H.; Jiang, B.; Lu, X.; Ding, W. Effects of tantalum content on the structure stability and oxygen permeability of BaCo0.7Fe0.3−xTa0.1O3−δ ceramic membrane. Int. J. Hydrogen Energy 2013, 38, 11090–11096. [CrossRef]

60. Cheng, H.; Luo, L.; Yao, W.; Lu, X.; Zou, X.; Zhou, Z. Novel cobalt-free CO2-tolerant dual-phase membranes of Ce0.8Sm0.2O2–δ–Ba0.95La0.05Fe1−δZr0.2O3–δ for oxygen separation. J. Membr. Sci. 2015, 492, 220–229. [CrossRef]

61. Yi, J.; Weirich, T.; Schroeder, M. CO2 corrosion and recovery of perovskite-type BaCo1−x−yFe1−yNb1−yO3–δ membranes. J. Membr. Sci. 2013, 437, 49–56. [CrossRef]