



Article $Ce_{0.8}Y_{0.2}O_{2-\delta}$ -BaCe_{0.8} $Y_{0.2}O_{3-\delta}$ Dual-Phase Hollow Fiber Membranes for Hydrogen Separation

Yuepeng Hei¹, Zuojun Lu¹, Claudia Li², Jian Song^{1,*}, Bo Meng¹, Naitao Yang¹, Sibudjing Kawi², Jaka Sunarso^{3,*}, Xiaoyao Tan⁴ and Shaomin Liu⁴

- ¹ Department of Chemical Engineering, Shandong University of Technology, Zibo 255049, China; 13409804404@163.com (Z.L.)
- ² Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117585, Singapore
- ³ Research Centre for Sustainable Technologies, Faculty of Engineering, Computing and Science, Swinburne University of Technology, Jalan Simpang Tiga, Kuching 93350, Sarawak, Malaysia
- ⁴ State Key Laboratory of Separation Membranes and Membrane Processes, Department of Chemical Engineering, Tiangong University, Tianjin 300387, China; tanxiaoyao@tiangong.edu.cn (X.T.)
- * Correspondence: jian.song@sdut.edu.cn (J.S.); jsunarso@swinburne.edu.my or barryjakasunarso@yahoo.com (J.S.); Tel.: +86-533-2181681 (J.S.); +60-82260709 (J.S.)

Abstract: Partial oxidation of methane (POM) is a prominent pathway for syngas production, wherein the hydrogen in syngas product can be recovered directly from the reaction system using a hydrogen (H_2) -permeable membrane. Enhancing the efficiency of this H_2 separation process is a current major challenge. In this study, $Ce_{0.8}Y_{0.2}O_{2-\delta}$ -BaCe_{0.8} $Y_{0.2}O_{3-\delta}$ (YDC-BCY) hollow fiber (HF) membranes were developed and characterized for their H₂ permeation fluxes. Firstly, YDC and BCY ceramic powders were synthesized using the sol-gel method, followed by the fabrication of YDC-BCY dualphase ceramic HF membranes using a combined phase inversion-sintering process. Characterization using SEM, powder XRD, EDS, and electrical conductivity tests confirmed the phases of the prepared powders and HF membranes. Well-structured YDC and BCY powders with uniform particle sizes were obtained after calcination at 900 °C. With the addition of 1 wt.% Co₂O₃ as a sintering aid, the YDC-BCY dual-phase HF membrane achieved densification after sintering at 1500 °C. Subsequently, the influences of sweep gas composition and temperature on the hydrogen permeation of the YDC-BCY HF membranes with YDC/BCY molar ratios of 2:1, 3:1, and 4:1 were investigated. At 1000 °C and a sweep-gas flow rate of 120 mL·min⁻¹, the YDC-BCY HF membrane with a YDC/BCY molar ratio of 4:1 exhibited a peak hydrogen flux of 0.30 mL \cdot min⁻¹ cm⁻². There is significant potential for improving the hydrogen permeation of dual-phase ceramic membranes, with future efforts aimed at reducing dense layer thickness and enhancing the membrane material's electronic and proton conductivities.

Keywords: sintering aid; sol-gel; phase inversion; dual-phase; syngas; POM

1. Introduction

Hydrogen (H₂) is a promising sustainable energy carrier to replace fossil fuels which has been extensively used in chemical production, such as ammonia and methanol [1–3]. Currently, H₂ is mainly produced through fossil fuel cracking and methane-reforming reactions, which mainly include the dry reforming of methane (DRM), steam reforming of methane (SRM), and partial oxidation of methane (POM), as shown in Figure 1. By using different methane-reforming methods, syngas with different CO/H₂ ratios can be obtained, which can be used for further industrial processes such as hydrogen separation, methanol preparation, and Fischer–Tropsch synthesis, depending on the actual conditions [4]. In the last decade, researchers have gradually studied methane double reforming [5,6] and



Citation: Hei, Y.; Lu, Z.; Li, C.; Song, J.; Meng, B.; Yang, N.; Kawi, S.; Sunarso, J.; Tan, X.; Liu, S. $Ce_{0.8}Y_{0.2}O_{2-\delta}$ -Ba $Ce_{0.8}Y_{0.2}O_{3-\delta}$ Dual-Phase Hollow Fiber Membranes for Hydrogen Separation. *Inorganics* **2023**, *11*, 360. https://doi.org/ 10.3390/inorganics11090360

Academic Editor: Elsa Lasseuguette

Received: 7 August 2023 Revised: 27 August 2023 Accepted: 30 August 2023 Published: 1 September 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). triple reforming reactions [7–10] on the basis of single reforming. This type of multireforming reaction process is more complex with more side reactions. The introduction of gas separation membranes into the reactor not only allows for precise control of the feed of reactants and the extraction of products to control the progress of the reaction, but also achieves an even distribution of gases on the permeate side and avoids the occurrence of hot-spots. Syngas production via POM is one of the most suitable reactions for industrial hydrogen production due to its mildly exothermic reaction, which avoids the high energy consumption that may result from other reforming reactions [11].



Figure 1. Classification of methane reforming.

However, the products of POM are H_2 -containing gas mixtures that require further separation and purification to obtain pure H₂ [12]. Various technologies are employed for H₂ separation and purification, including pressure swing adsorption, cryogenic separation, and membrane separation [1,13]. Among these, membrane separation stands out by utilizing the selective permeability of membranes to separate H_2 . Compared with the other methods, membrane separation offers advantages such as a compact equipment footprint, simplified operation, and reduced operation costs and energy consumption [14,15]. Membrane separation can be categorized into three types based on the membrane material: organic, metallic, and ceramic membranes. Although organic membranes have been used commercially, their mechanical stability in corrosive atmospheres, such as HCl, SO_x , and CO_2 , is limited [13]. Metallic membranes, especially Pd and its alloys, effectively separate and purify H_2 at a temperature range of 300–600 $^{\circ}C$ to obtain high-purity H₂. However, they suffer from irreversible phase transitions and degradation after multiple thermal cycles, leading to membrane failure [13]. In contrast, at high temperatures, mixed protonic-electronic conducting (MPEC) ceramic membranes exhibit a theoretical H₂ selectivity of up to 100% and do not require external circuits. MPEC membranes outperform the other membranes with their superior strength and excellent chemical and physical stabilities [1,16,17]. When used in sustained product-separation membrane reactors, MPEC hydrogen-permeable ceramic membranes are capable of selectively separating hydrogen to the permeate side to accomplish enrichment, which can not only purify the product but also enable the reversible reaction to proceed in the desired direction. In addition, MPEC hydrogen-permeable ceramic membranes can also be used in multi-reaction coupled membrane reactors. Reactions take place on both sides of the membrane in this type of membrane reactor, and the products of the reaction on one side of the membrane happen to be the raw materials of the reaction on the other side; the membrane has selective permeability to this material. Hence, a certain product from one side of the membrane permeates to the other side and is consumed by another reaction, causing the two reactions to promote each other, greatly improving the conversion rate of the two reactions.

MPEC membrane materials typically comprise alkaline earth metal-containing perovskite-type oxides, with ABO₃-type perovskite oxides being the most commonly used. In these materials, the B-site ions are partially replaced by trivalent cations, generating oxygen vacancies to maintain electrical neutrality [18]. The presence of oxygen vacancies and electron defects allows them to react with hydrogen, leading to the generation of protonated lattice oxygen, which confers protonic conductivity to the material. Perovskites also exhibit electronic conductivity as their cations undergo valence changes in reducing atmospheres [14]. Despite the promising features of MPEC ceramic membranes, their practical application is hindered by low hydrogen permeation and instability under a reducing atmosphere. Researchers are actively addressing this challenge by exploring various modification strategies, including optimizing material compositions and membrane structures [1,14,17].

In terms of material compositions, the oxygen vacancies, the ratio of variable valence ions, and the basicity of the material can be adjusted using elemental doping strategies, which in turn improve the protonic–electronic mixed conductivity as well as the resistance to acid gases such as carbon dioxide. In some perovskite solid solution systems, non-systematic changes in structural parameters occur due to the cation deficiencies or substitutions, as observed in A-site deficient $Sr_{1-x}Ce_{0.9}Yb_{0.1}O_{3-\delta}$ [19]. A-site deficiency results in the formation of A-site cation defects and oxygen vacancies as follows:

$$Sr_{Sr}^{\times} + O_o^{\times} \to V_{Sr}'' + V_o^{\cdots} + SrO$$
⁽¹⁾

This decreases the chemical potential of alkaline ions in the A-site, reducing their susceptibility to carbonation. In addition, the presence of unreacted alkaline oxides present at grain boundaries is minimized, thereby enhancing the chemical stability of the material. Furthermore, electronic conduction can be regulated by doping with multivalent cations, facilitating the transfer of free electrons between low- and high-oxidation-state cations [20]. In addition to elemental doping, the preparation of composite materials offers an effective strategy to optimize the fluxes in hydrogen-permeable ceramic membranes. Single-phase BaCeO₃ or SrCeO₃ ceramic membranes doped with rare earth or transition metal elements suffer from limited electronic conductivity, hampering high hydrogen permeation flux. Therefore, researchers have turned to dual-phase composite membranes, introducing metals as electronic conducting phases to enhance hydrogen permeation flux [21]. Ni was used as an electronic conductor and catalyst to boost the electronic conductivity and the surface-exchange reactions. However, Ni is prone to carbon accumulation, which severely limits the application of ceramic membranes. Although the addition of a metal phase optimizes the hydrogen permeation flux of the ceramic membrane, the difference in the thermal expansion coefficients between metals and ceramics and the metal oxidation reduces the thermo-mechanical stability and densification of metal-ceramic dual-phase membranes [22]. Moreover, the interactions between metals and ceramics occur at high temperatures, especially the interdiffusion between ions, complicating the preparation of metal–ceramic dual-phase membranes [23,24].

The preferred strategy for the preparation of dual-phase composite membranes involves transitioning the second phase to a ceramic phase with good electronic conductivity. This strategy enhances the electronic conductivity of the material and decreases the thermal expansion mismatch between the electron-conducting phase and the proton-conducting phase. Fabricating ceramic–ceramic dual-phase membranes simplifies the process without needing inert or reducing gas protection [25]. Rare-earth-doped CeO₂ improves the chemical stability and offers both oxygen ion conduction and desirable electronic conductivity [26]. As for the membrane structure, an asymmetric design with independent proton–electron conductive phase distribution, including a porous support layer and ultra-thin dense layer, enhances the hydrogen permeability and stability [27–30]. Forming continuous proton-conducting and electron-conducting phases in dual-phase ceramic membranes is an effective strategy to improve the hydrogen permeation performance of ceramic membranes [31]. This membrane benefited from the low bulk-phase diffusion resistance and minimal interaction between phases due to their uniform distribution.

The hydrogen permeation mechanism in ceramic hydrogen-permeable membranes is governed by bulk diffusion and surface-exchange reactions. Enhancing hydrogen permeation involves reducing the membrane thickness and adjusting the surface structure, which is often achieved using asymmetric membranes with thin dense layers and porous support layers. Hollow fiber (HF) membranes, particularly with around 200-µm thick transport layers, offer advantages in high-temperature sealing and effective membrane area per unit volume [20,32,33]. Dual-phase HF membranes with thin dense layers benefit from the phase inversion-sintering technique, synergizing reduced membrane thickness and increased surface reaction rates to enhance perovskite ceramic membrane hydrogen permeation [34]. This work focuses on synthesizing high-purity, small-size, and uniform $Ce_{0.8}Y_{0.2}O_{2-\delta}$ (YDC) and BaCe_{0.8} $Y_{0.2}O_{3-\delta}$ (BCY) ceramic powders through the sol-gel route, and fabricating YDC-BCY dual-phase HF membranes using a combined phase inversion-sintering process. The structure and hydrogen permeation fluxes of the YDC-BCY dual-phase MPEC ceramic hydrogen-permeable membrane were systematically investigated. The influence of synthesis conditions on the hydrogen permeability of the HF membrane was examined, and the optimal synthesis process and parameters of ceramic powders and HF membranes, as well as the relationship between the membrane structure and the hydrogen fluxes, were determined, serving as a foundation for membrane reactor development.

2. Experimental Section

2.1. Synthesis of YDC-BCY Dual-Phase Ceramic Powders

YDC and BCY powders were synthesized using the sol-gel method [35,36]. Taking the preparation of 0.1 mol YDC and BCY as an example, the required amounts of raw materials are shown in Table 1. The synthesis process involved adding $Ba(NO_3)_2$, $Ce(NO_3)_3 \cdot 6H_2O$, and Y(NO₃)₃·6H₂O in a stoichiometric ratio to a mixture of 100 mL ammonia and 100 mL deionized water at 80 °C under stirring. Ethylene glycol and citric acid were used as chelating agents for the YDC powder precursor, according to the molar ratio of total metal ions/ethylene glycol/citric acid of 1:1:2. For the BCY powder precursor, glycine was employed as the chelating agent, promoting dissolution of Ba²⁺ and serving as a combustion aid. Following water evaporation, a dark-brown gel gradually formed, and after adding ammonia and stirring for 15 min, the gel was heated to 380 °C in a stainless-steel container for further water evaporation and spontaneous combustion, yielding YDC and BCY powder precursors. The obtained powder precursors were placed into crucibles and calcined at 900 °C for 5 h to burn off the residual organic matter and to obtain the ceramic powders. The powders were then wet milled using anhydrous ethanol as a dispersant in a planetary ball mill for 48 h with a molar ratio of YDC/BCY of 2:1, 3:1, and 4:1, respectively. The YDC-BCY mixed powders with homogeneous particle size were dried and sieved with a 200-mesh sieve. Additionally, during ball milling, a portion of the powder was combined with 1.0 wt.% cobalt (III) oxide (Co_2O_3) as a sintering additive to investigate the effect of the sintering additive on the membrane densification.

Table 1. Composition of raw materials required for the preparation of 0.1 mol BCY and YDC powder.

Materials	BC	CY	YDC		
	Quantity/mol	Quantity/g	Quantity/mol	Quantity/g	
BaNO ₃	0.10	26.13	0.00	0.00	
$Ce(NO_3)_3 \cdot 6H_2O$	0.08	34.73	0.08	34.73	
$Y(NO_3)_3 \cdot 6H_2O$	0.02	7.66	0.02	7.66	
Ethylene glycol	0.00	0.00	0.20	12.41	
Citric acid monohydrate	0.00	0.00	0.40	84.06	
Glycine	0.40	30.03	0.00	0.00	
Water	5.56	100 (mL)	5.56	100 (mL)	
Ammonia	-	100 (mL)	-	100 (mL)	

2.2. Fabrication of YDC-BCY Dual-Phase HF Membrane

The YDC-BCY HF membrane was prepared using a combined phase inversionsintering process [37,38]. The specific parameters to fabricate the YDC-BCY HF membrane are summarized in Table 2. The fabrication process of the HF membrane involved the following steps: polyethersulfone (PESf) was dissolved in 1-methyl-2-pyrrolidinone (NMP) with a PESf/NMP mass ratio of 1:4 under stirring to form a light-yellow transparent solution. Then, ceramic powder, either with or without 1.0 wt.% Co₂O₃, was added to the solution in a PESf to powder mass ratio of 1:10, and the mixture was continuously stirred for 48 h to achieve a uniform casting solution. The casting solution was introduced into a stainless-steel cylinder and subjected to a 1.5 h vacuum degassing treatment. After degassing, the stainless-steel cylinder was connected to compressed nitrogen and pressurized to 0.1 MPa. Deionized water and tap water were used as the internal and external coagulants, respectively. The flow rate of the internal coagulation bath was 30 mL min⁻¹. The HF membrane precursor obtained by spinning was fully solidified in the external coagulation bath for 24 h. After solidification, the HF membrane precursor was cut into small sections of 45–50 cm in length, followed by straightening at both ends, and allowed to dry in air. The HF membrane precursor was then sintered in a high-temperature furnace with a heating and cooling rate of 2 $^{\circ}$ C min⁻¹, and the dwell time at sintering temperature was 5 h.

Table 2. Fabrication parameters of YDC-BCY HF membrar	ne.
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Experimental Parameters	Values	
Composition of the spinning solution (wt.%)		
YDC-BCY	61.54	
NMP	30.77	
PESf	7.69	
Extrusion pressure (MPa)	0.1	
Air gap distance (cm)	0	
Spinning suspension flow rate (mL min ^{-1})	5.0	
Internal coagulant flow rate (mL min $^{-1}$)	30	
Sintering temperature (°C)	1500, 1550	
Dwelling time at sintering temperature (h)	5	
Heating/cooling rate ($^{\circ}C \min^{-1}$)	2	

2.3. Characterization

The crystalline structure of the materials was characterized using a powder X-ray diffractometer (XRD, D8-Advance, Bruker, Mannheim, Germany) equipped with a Cu-K α ray source ($\lambda = 0.15404$ nm), operating at tube voltage and current of 40 kV and 30 mA, respectively. The scanning range spanned 20–80° with a scanning speed of 8° min⁻¹. Microstructural analysis of the powder and HF membranes was conducted using a field-emission scanning electron microscope (FESEM, Apreo, Thermo Scientific, Waltham, MA, USA), or a scanning electron microscope (SEM, EM-30^N, COXEM, Daejeon, Republic of Korea). Energy-dispersive spectroscopy (EDS) was used to analyze the elemental distribution on the material surface. Gold spraying was conducted prior to SEM characterization.

The four-electrode direct current (DC) method was used to measure the electrical conductivity of the samples at different temperatures and atmospheres (nitrogen and hydrogen), within the range of 600–850 °C with a temperature interval of 50 °C. For electrical conductivity tests, 1.4 g of YDC-BCY powder was pressed into a cuboid shape with a stainless-steel mold (30 mm × 8 mm × 4 mm) under static pressure, followed by sintering at 1400 °C for 3 h. Double-stranded silver wires were attached to the ends of the cuboid sample and secured with silver paste that also functioned as current-voltage collecting electrodes. Conductivity measurements were performed using a digital source meter (Keithley 2400, Cleveland, OH, USA). During tests, the current was varied from 0.00 mA to 10.00 mA, leading to corresponding voltage changes based on current and temperature.

Each condition was tested three times to take the average value. The conductivity was calculated using Equation (2), given below:

С

$$r = \frac{L}{RS}$$
(2)

where *L* is the effective length of the sample, cm; *S* is the cross-sectional area of the sample, cm²; and *R* is the resistance of the sample, Ω .

The mechanical strength was obtained using a mechanical testing machine (WDW-500 N, Jinan Zhongluchang Testing Machine Manufacturing Co., Ltd., Jinan, China) via a three-point bending method and was calculated as follows:

$$\sigma_F = \frac{8FLD}{\pi(D^4 - d^4)} \tag{3}$$

where σ_F is the mechanical strength, MPa; *F* is the critical force at which sample fracture took place, N; *L* is the span distance of the sample, fixed at 30 mm in this experiment; and *D* and *d* are the outer and inner diameters of the HF membrane, respectively, mm.

2.4. Hydrogen Permeation Flux of YDC-BCY Dual-Phase HF Membrane

Dense HF membranes were assembled into membrane reactors, using fittings to connect and isolate the atmosphere of shell side from fiber lumen. Hydrogen permeation tests were performed with H₂-He mixture as the feed gas in the shell side and N₂ as the sweep gas in the fiber lumen. The flow rate of the gas was calibrated using a soap bubble flow meter. The reactor was fixed in a tube furnace and stabilized for about 15 min after heating to target temperature before testing. The exhaust of sweep gas was connected to a gas chromatograph (GC, 6890N, Agilent, Santa Clara, CA, USA) to detect the gas composition, and the hydrogen permeation flux through the HF membrane was calculated according to Equations (4) and (5):

$$J_{H_2} = \frac{F(x_{H_2} - x_{H_e})}{A_m}$$
(4)

$$A_m = \frac{\pi l(D-d)}{\ln(\frac{D}{d})} \tag{5}$$

where J_{H_2} is the permeation flux of hydrogen, mL min⁻¹ cm⁻²; *F* is the exhaust gas flow rate of N₂ sweep gas, mL min⁻¹; and x_{H_2} and x_{He} are the hydrogen and helium concentration detected by GC, %. A_m is the effective area of the membrane, cm²; *D* and *d* are the outer diameter and inner diameter, respectively, of the membrane, cm; and *l* is the effective length of the YDC-BCY membrane, which is equal to the length of the thermostatic zone, i.e., 5 cm.

3. Results and Discussion

3.1. Crystalline Structure and Morphology of YDC-BCY Dual-Phase Ceramic Powders

Figure 2 shows the powder XRD patterns of BCY and YDC powders calcined at 900 °C and YDC-BCY HF membranes with 1.0 wt.% Co_2O_3 as a sintering additive sintered at 1500 °C. Comparative analysis with the Powder Diffraction File (PDF) cards for YDC (PDF#:01-075-0175) and BCY (PDF#:04-011-8649) [39] revealed that the YDC and BCY powders corresponded to the fluorite and perovskite phases, respectively, exhibiting no other secondary peaks. This suggests that the powders attained pure phases after 5 h of calcination at 900 °C. The powder XRD patterns of the three HF membranes, with varying molar ratios of YDC/BCY of 2:1, 3:1, and 4:1, displayed diffraction peaks at 20 of 33.1° , 47.5° , 56.5° , and 76.7° , corresponding to the fluorite phase of YDC, and at 20 of 41.1° , 50.8° , 59.4° , and 67.5° , corresponding to the cubic perovskite phase of BCY. No additional diffraction peaks were observed. Despite the addition of sintering additive at a mere 1.0 wt.%, no corresponding crystal diffraction peaks were detected in the patterns. A

comparison between the patterns of the calcined powders and the sintered HF membranes substantiates three key points: (1) High-temperature sintering at 1500 °C did not lead to chemical reactions between the YDC and BCY phases, confirming their good chemical compatibility. (2) The sintering additive did not compromise the integrity of the YDC and BCY phases during the sintering process. (3) As the molar ratio of YDC and BCY powder in the YDC-BCY HF membrane increased from 2:1 to 4:1, the diffraction peak intensity of the BCY perovskite phase decreased, while the intensity of the YDC fluorite phase gradually increased.



Figure 2. Powder XRD patterns of YDC and BCY powders and YDC-BCY HF membranes.

Figure 3 depicts the SEM images of the YDC and BCY powders, along with the 4:1 YDC-BCY powder mixture, accompanied by EDS mapping of the 4:1 YDC-BCY powder mixture. In Figure 3A–C, it is evident that the small particles in the YDC and BCY powders had a particle size of less than 1 μ m, and the fine particles in all the samples coalesced into larger agglomerates due to the decreased surface energy resulting from particle interaction and agglomeration. The diameter of the YDC aggregates was 5–10 μ m, while the diameter of the BCY aggregates was 1–5 μ m. It is clear that the diameter of the YDC aggregates was larger. These larger agglomerates can be further reduced into fine particles through subsequent ball milling treatments. By examining the elemental distribution of Ba with that of Ce and Y in Figure 3D, a uniform and continuous distribution of the YDC and BCY phases is discernible. This consistent distribution facilitated rapid carrier transport. Furthermore, the elements were uniformly dispersed within their corresponding phases without distinct segregation regions, which also proved the stability of the material. In addition, Figure 3C,D show that the BCY and YDC powders can still be basically distinguished in the mixture by SEM morphology and elemental distribution.



Figure 3. SEM images of **(A)** YDC, **(B)** BCY, and **(C)** 4:1 YDC-BCY powder mixture, and **(D)** EDS of 4:1 YDC-BCY powder mixture.

3.2. Particle Size Distributions and Electrical Conductivities of YDC-BCY Dual-Phase Ceramic Powders

The particle size distributions of the YDC and BCY powders synthesized using the sol-gel method, along with YDC-BCY powder mixtures at three different YDC/BCY molar ratios of 2:1, 3:1, and 4:1, are shown in Figure 4. It is evident that the particle size of the powders synthesized using the sol-gel method was in the nanometer range. This could be attributed to the significant gas release during the gel combustion process, leading to the formation of porous structures, which consequently reduced the particle sizes. In addition, the particle size of the YDC powder was smaller than that of the BCY powder, and the particle size of the YDC-BCY powder mixture decreased with the increase in the content of YDC powder. For instance, the average particle sizes of the YDC and BCY powders were mixed in molar ratios of 2:1, 3:1, and 4:1, the resulting powder particle sizes ranged from 255 to 615 nm, 190 to 295 nm, and 164 to 255 nm, respectively. Corresponding average particle sizes proved advantageous for fabricating dense hollow fiber (HF) membranes, allowing for lower sintering temperatures, reduced energy consumption, and cost savings.

Figure 5 illustrates the electrical conductivities of three distinct compositions of sintered YDC-BCY cuboids (YDC/BCY molar ratios of 2:1, 3:1, and 4:1). As shown, the conductivities of the three distinct compositions in H₂ and N₂ atmospheres show an increasing trend with the increase in the YDC/BCY molar ratio. Under the N₂ atmosphere, the materials displayed electronic conduction. Notably, the electronic conductivity of all three materials remained low, measuring below 0.1 S cm⁻¹. Upon transitioning to a H₂ atmosphere, the conductivity of the three materials experienced varying degrees of increase, showcasing a combination of both electron and proton conduction, and the proton conduction played the leading role. The conductivity of all three materials increased with a rise in temperature from 600 to 850 °C and showed strong protonic conductivity. At 850 °C, the YDC-BCY material with a YDC-BCY molar ratio of 3:1 exhibited the highest conductivity of 0.31 S cm⁻¹. It is known that the electrical conductivity links to the results of the membrane's potential H₂ permeation; hence, the combined proton and electronic conduction should be as high as possible so as to achieve a high H₂ permeation flux.



Figure 4. Particle size distribution of YDC, BCY, and YDC-BCY powder mixtures (YDC/BCY molar ratios of 2:1, 3:1, and 4:1).



Figure 5. Temperature-dependent electrical conductivities of YDC-BCY materials with different YDC/BCY molar ratios of 2:1, 3:1, and 4:1 under N₂ and H₂ atmospheres.

3.3. Morphologies of YDC-BCY Dual-Phase HF Membranes

Figure 6 shows the effect of a cobalt (III) oxide (Co_2O_3) sintering additive on the surface morphologies of 4:1 YDC-BCY HF membranes. When the YDC-BCY dual-phase ceramic HF membranes with a molar ratio of 4:1 were sintered without a sintering additive, a dense membrane structure could not be achieved even at a sintering temperature of 1550 °C. As shown in Figure 6(A1,A2), the inner and outer surfaces of the YDC-BCY HF membrane still had numerous holes, and thus were unsuitable for the hydrogen permeation test. In addition, elevated sintering temperatures not only increased the energy consumption, but also risked over-sintering the ceramic material. In contrast, Figure 6B shows the microstructure of the HF membranes after sintering with the addition of 1.0 wt.% Co_2O_3 at 1500 °C. Co_2O_3 acted as a sintering aid, which significantly lowered the sintering temperature of the sintered YDC-BCY HF membranes with 1.0 wt.% Co_2O_3 were structurally dense, which was further corroborated by gas tightness testing of the sintered membranes. The YDC-BCY fluorite-perovskite oxide grain was small in size with a high surface energy, and the grains gradually grew with temperature. Co_2O_3 was amorphous and easy to

decompose at high temperatures. Therefore, it was beneficial for the densification and sintering of YDC-BCY fluorite-perovskite [40]. In addition, the amount of Co_2O_3 was a mere 1.0 wt.%, which was so insignificant that the impact on the crystal structure of the membrane was not apparent.



Figure 6. Surface morphology of 4:1 YDC-BCY HF membranes after sintering ((**A**) sintered at 1550 °C without a sintering aid; (**B**) sintered at 1500 °C with 1.0 wt.% Co_2O_3 as a sintering aid; **1**, inner surface; **2**, outer surface).

The cross-section and surface morphologies of YDC-BCY dual-phase ceramic HF membranes with three different molar ratios (YDC/BCY molar ratios of 2:1, 3:1, and 4:1) sintered at 1500 °C with a 1.0 wt.% sintering additive are shown in Figure 7. The membrane walls of these HF membranes exhibited distinctive features, as shown in Figure 7(A1,B1,C1). The central and near-surface regions of the membrane walls displayed dense structures, with finger-like pore layers sandwiched between them. This configuration contributed to an evident asymmetric membrane-wall structure, facilitating the conduction of hydrogenoxygen species and enhancing hydrogen permeation. The thicknesses of dense separation layers and finger-like pore layers were almost the same; each occupied half of the total thickness of the membrane wall. The porosity gradually decreased with the increment of YDC/BCY from 2:1 to 4:1. Additionally, there were no potential defects or irregularities observed in the membrane walls and surfaces. The inner and outer surfaces of the HF membranes were dense, as shown in Figure 7(A2,A3,B2,B3,C2,C3). The grains exhibited a closely packed arrangement with well-defined grain boundaries, showcasing two crystal structures with distinct grain sizes. As the molar ratio of YDC-BCY increased, the content of the YDC phase in the membrane increased. At the same temperature, YDC was more prone to sintering than BCY, so the particle size of YDC was larger than that of BCY (as demonstrated by EDS mapping on the membrane surface after the stability test). Therefore, there were more YDC with large particle sizes on the membrane surface, while there were fewer BCY with smaller particle sizes.



Figure 7. Cross-section and surface morphologies of YDC-BCY HF membranes sintered with the addition of 1.0 wt.% Co_2O_3 (YDC/BCY = (**A**) 2:1, (**B**) 3:1, and (**C**) 4:1; **1**, membrane wall; **2**, inner surface; **3**, outer surface).

Figure 8 shows the mechanical strengths of YDC-BCY HF membranes with different YDC/BCY molar ratios. The mechanical strength of the HF membrane gradually increased with the increase in the molar ratio. The YDC-BCY HF membrane with a molar ratio of 4:1 reached maximum mechanical strength after sintering at 1500 °C, reaching 188.95 MPa. During the phase inversion spinning process, there were sponge-like and finger-like pores in the membrane wall. As the sintering process progressed, organic compounds such as PESf in the membrane structure decomposed, and the grains also began to fuse and grow as the temperature increased, causing the micropores between the grains to gradually decrease. This reduced the porosity of the membrane and increased its mechanical strength. When the dense layer and sponge-like pores of the membrane were completely filled with growing grains, the HF membrane became dense. Continuing to increase the sintering temperature may lead to over-sintering and melting of the membrane, resulting in a decrease in its mechanical strength. Therefore, based on SEM characterization and gas tightness measurement results, the sintering temperature of YDC-BCY HF was determined to be 1500 °C.



Figure 8. Mechanical strength of YDC-BCY HF membranes sintered at 1500 °C with the addition of 1.0 wt.% Co_2O_3 (molar ratios of YDC/BCY = 2:1, 3:1, and 4:1).

3.4. Hydrogen Permeation of YDC-BCY Dual-Phase HF Membranes

The evaluation of hydrogen permeation fluxes for the three different YDC-BCY HF membranes involved flowing a mixture of H_2 and H_2 through the shell side at a flow rate of 15–15 mL min⁻¹, while N₂ flowed through the fiber lumen, with the results as shown in Figure 9. The temperature had a great influence on the hydrogen permeation flux, where increased temperature led to improved gas diffusion, surface reactions, and bulk phase diffusion, resulting in a significant increase in the hydrogen permeation flux. For instance, considering the YDC-BCY HF membrane with a YDC/BCY molar ratio of 2:1, the hydrogen permeation flux at 1000 °C reached 0.20 mL min⁻¹ cm⁻² under the flow rate of 120 mL min⁻¹ sweep gas, while the hydrogen permeation flux at 750 °C was only $0.03 \text{ mL min}^{-1} \text{ cm}^{-2}$. The change in the sweep-gas flow rate also affected the hydrogen permeation flux. With the increase in the sweep-gas flow rate, the hydrogen permeated to the sweep side was quickly removed by the sweep gas, elevating the surfaceexchange rate of the membrane. This, in turn, maintained a higher hydrogen partial pressure difference between the membrane's two sides, leading to increased hydrogen permeation due to the enhanced pressure gradient. However, this increase in permeation was limited, with the membrane's permeation rate stabilizing as the sweep-gas flow rate reached a certain threshold. This stabilization occurred because the rate-determining step of hydrogen permeation transitioned from the surface exchange to the bulk-phase diffusion. In addition, a study by Leng et al. [41] found that with the addition of sintering additive, more electron holes formed in the ceramic material, which was helpful for the proton conduction. At 900 °C, an improvement in the hydrogen permeation flux was obtained in this work compared with that of $0.08 \text{ mL min}^{-1} \text{ cm}^{-2}$ measured by Rosensteel et al. [39]. The conductivity of the dual-phase YDC-BCY materials is also one of the important factors affecting the permeation performance of the membrane. Figure 9 also shows the effect of the YDC/BCY ratio on the hydrogen permeation of ceramic dense HF membranes. It can be seen that the 1:4 BCY-YDC hollow fiber membrane had the highest hydrogen flux under the same conditions, and reached 0.30 mL min⁻¹ cm⁻² at 1000 °C. Based on the conductivities of the BCY-YDC materials with three different YDC/BCY ratios in different atmospheres shown in Figure 5, it can be found that the proton and electron mixed conductivity of the 1:4 BCY-YDC material was less than that of the 1:3 BCY-YDC material in a hydrogen-containing atmosphere. However, its electronic conductivity was the highest in N_2 . This revealed that the proton and electronic conductivity should match each other so as to reach high hydrogen permeation flux.



Figure 9. Hydrogen permeation performance of YDC-BCY dual-phase HF membranes with different molar ratios ((**A**) 2:1, (**B**) 3:1, (**C**) 4:1).

The hydrogen permeation flux of the dual-phase MPEC material was also affected by the ratio of its two phases. From Figure 9, the 4:1 YDC-BCY HF membrane had the highest hydrogen permeation flux under identical conditions. At 1000 °C and 120 mL min⁻¹ sweep gas, the hydrogen permeation reached 0.30 mL min⁻¹ cm⁻². By comparing the conductivities of the three compositions of YDC-BCY sintered cuboids in different atmospheres, as shown in Figure 5, it becomes evident that the proton–electron mixed conductivity of the 4:1 YDC-BCY material was lower than that of the 3:1 YDC-BCY material in the hydrogen atmosphere. However, its electronic conductivity was the highest in the N₂ atmosphere, aligning with the hydrogen permeation requirement of MPEC hydrogenpermeable membrane, which necessitates a matching of proton and electron conductivities.

Acid gases such as CO_2 would be adsorbed on the feed surface of the hydrogen permeation membrane, hindering surface-exchange reactions, thereby affecting the proton permeation and even corroding the hydrogen permeation membrane, reducing its mechanical strength. In industrial applications, hydrogen permeation membranes are required to have good resistance to acidic atmospheres. Therefore, the effect of CO_2 on the hydrogen permeation and short-term hydrogen permeation stability of the 4:1 YDC-BCY HF membranes in CO_2 -containing atmospheres was tested, the result of which is shown in Figure 10.



Figure 10. (**A**) Hydrogen permeation fluxes of 4:1 YDC-BCY HF membrane at different temperatures and CO₂ concentrations (H₂-He/CO₂ = 15–15 mL·min⁻¹, N₂ + CO₂ = 60 mL·min⁻¹); (**B**) short-term hydrogen permeation stability of 4:1 YDC-BCY HF membrane.

The results indicated that the increase in hydrogen permeation flux when CO₂ was used as the sweep gas was due to the presence of a reverse water–gas shift (RWGS) reaction on the sweep side, which consumed H₂, reduced the H₂ partial pressure on the sweep side, and increased the partial pressure gradient between the feed side and the sweep side. This reaction is thermodynamically advantageous and may occur on the membrane surface above 750 °C [33]. CO was also detected in the sweep gas, and water droplets were also observed in the cold trap used to condense steam in the gas flow to prevent water from entering the GC. The decrease in hydrogen permeation when CO₂ was in the feed gas was

attributed to the adsorption of CO_2 on the membrane surface, which reduced the surface active-sites of hydrogen and hindered its adsorption, thereby affecting the surface-exchange reaction. It was not because the YDC-BCY hydrogen-permeable membrane underwent a chemical reaction with CO_2 to generate carbonates, causing irreversible damage to the membrane structure. Therefore, hydrogen permeation could be restored with the removal of CO_2 . This can also be verified via SEM and EDS characterization of the hydrogen-permeable membrane after the stability test.

In Table 3, the highest H_2 flux of the 4:1 YDC-BCY HF membrane in this work is compared with those of some representative ceramic composite membranes reported in the literature. As shown, the performance of the 4:1 YDC-BCY HF membrane is comparable with that of the reported work.

 Table 3. Hydrogen permeation flux comparison of 4:1 YDC-BCY HF membranes with reported composite membranes.

Membrane Composition	Thickness (mm)	T (°C)	Feed/Sweep Gas	H_2 Flux (mL min ⁻¹ cm ⁻²)	Ref.
$\begin{array}{c} Ce_{0.90}Gd_{0.10}O_{3-\delta}-\\ SrCe_{0.95}Fe_{0.05}O_{3-\delta}-\\ SrFe_{0.95}Ce_{0.05}O_{3-\delta}\end{array}$	0.7	940	40% H ₂ /wet Ar	0.54	[26]
$SrCe_{0.95}Fe_{0.05}O_{3-\delta}$ - $SrCe_{0.05}Fe_{0.05}O_{2-\delta}$	0.7	900	$40\% H_2$ /wet Ar	0.33	[42]
$SrZrO_{3-\delta}$ - $SrFeO_{3-\delta}$	1.0	900	H ₂ /wet Ar	0.048	[43]
BaCe _{0.65} Zr _{0.2} Y _{0.15} O _{3-δ} - Gdo 15Ceo 85O _{2-δ}	0.65	755	Wet 50% H_2 /wet Ar	0.27	[44]
$BaCe_{0.8}Eu_{0.2}O_{3-\delta} - Ce_{0.8}Y_{0.2}O_{2-\delta} \\BaCe_{0.8}Y_{0.2}O_{3-\delta} - Ce_{0.8}Y_{0.2}O_{2-\delta}$	0.5 1.44	700 900	Dry 50% H ₂ /wet Ar 10% H ₂ /Ar	0.61 0.0744	[45] [39]
BaCe _{0.85} Fe _{0.15} O _{3-δ} - BaCe _{0.15} Fe _{0.85} O _{3-δ}	1	950	$50\% H_2/Ar$	0.76	[46]
$BaCe_{0.2}Zr_{0.7}Y_{0.1}O_{3-\delta}$ - $Sr_{0.95}Ti_{0.9}Nb_{0.1}O_{3-\delta}$	1	700	Wet 50% $H_2/wetAr$	0.011	[47]
$La_{5.5}WO_{11.25\mbox{-}\delta}\mbox{-}La_{0.87}Sr_{0.13}CrO_{3\mbox{-}\delta}$	0.37	700	Wet 50% H ₂ /wet Ar	0.15	[48]
$Ce_{0.8}Y_{0.2}O_{2-\delta}$ -Ba $Ce_{0.8}Y_{0.2}O_{3-\delta}$	0.2	900	$50\% H_2/N_2$	0.21	This work

3.5. Post-Test Characterization

Figure 11A displays a comparison of the powder XRD patterns of YDC-BCY HF membranes with a YDC/BCY molar ratio of 4:1 before and after hydrogen permeation tests. The crystalline phase structure of the YDC-BCY fluorite-perovskite remained unchanged after hydrogen permeation, indicating stability without new diffraction peaks or phase alterations. The SEM images in Figure 11B,C show minimal changes to the inner and outer surfaces of the dual-phase HF membranes (compared with Figure 7(C2,C3)), maintaining their dense structure. This confirms the membranes' stability and resistance to high-temperature reduction in a hydrogen-containing atmosphere.



Figure 11. (**A**) Powder XRD patterns and (**B**,**C**) SEM images of 4:1 YDC-BCY HF membrane after hydrogen permeation test: (**B**) inner surface; (**C**) outer surface.

In Figure 12, the surface SEM of the sweep side shows that using a mixture of CO₂containing gas as the sweep gas, the surface morphology of the membrane was no longer smooth, making it easy to distinguish two-phase particles. The rough particles should belong to the BCY phase, while the particles that remained smooth should belong to the YDC phase. However, the membrane surface still maintained a dense structure without cracks due to the attack of CO_2 , which can be attributed to the presence of the YDC phase limiting the reaction between the BCY phase and CO_2 . The distribution of the Ba element on the surface of the sweep side was basically the same as the distribution of small particles with rough surfaces, indicating that only the BCY phase reacted with CO_2 , which was also the reason why the stability of the dual-phase membrane was better than that of the single-perovskite-phase membrane.



Figure 12. Inner surface SEM image and EDS mapping of 4:1 YDC-BCY HF membrane after hydrogen permeation stability test.

4. Conclusions

In this work, YDC and BCY ceramic powders were successfully synthesized using the sol-gel method. Dual-phase YDC-BCY HF hydrogen-permeable membranes were then fabricated through a combined phase inversion–sintering technique, followed by an investigation into the membrane performance and influencing factors. The key findings are outlined below:

- YDC and BCY powders with fluorite and perovskite phases, respectively, were successfully synthesized using citric acid-ethylene glycol and glycine as chelating agents, followed by calcination at 900 °C for 5 h.
- The addition of 1.0 wt.% Co₂O₃ as a sintering additive significantly lowered the sintering temperature, resulting in dense YDC-BCY HF hydrogen-permeable membranes after sintering at 1500 °C for 5 h.
- Temperature, sweep gas, and molar ratio of YDC/BCY had a significant effect on the hydrogen permeation flux of HF membranes. At 1000 °C, the HF membrane with a BCY/YDC molar ratio of 4:1 exhibited the highest hydrogen permeation flux of 0.30 mL min⁻¹ cm⁻², which was 1.5 times higher than that of the HF with a BCY/YDC molar ratio of 2:1.
- The hydrogen separation efficiency achieved by a single hydrogen-permeable membrane was limited. In future work, integrating multiple hydrogen-permeable membranes and collecting permeated hydrogen by vacuum could enhance the separation efficiency and purity.

Author Contributions: Y.H.: Data Curation, Validation, Investigation, Methodology. Z.L.: Data Curation, Validation, Investigation, Writing—Original draft. C.L.: Writing—Review and editing. J.S. (Jian Song): Supervision, Funding acquisition, Conceptualization, Writing—Review and editing. B.M.: Supervision, Project administration, Conceptualization. N.Y.: Project administration. S.K.: Funding acquisition, Project administration. J.S. (Jaka Sunarso): Supervision, Project administration, Writing—Review and editing. Writing—Review and editing. X.T.: Funding acquisition, Project administration. S.L.: Funding acquisition, Project administration. All authors have read and agreed to the published version of the manuscript.

Funding: The authors gratefully acknowledge the research fundings provided by the National Natural Science Foundation of China (NSFC 22179073, 21805206, 22178271, and 22178015) and the Youth Innovation Team of Colleges and Universities in Shandong Province (2022KJ230). The authors appreciate the support from the National Research Foundation, Singapore; A*STAR, under its Low-

Carbon Energy Research (LCER) Funding Initiative (FI) Project (U2102d2011, WBS: A-8000278-00-00); and the Singapore Ministry of Education Academic Research Fund (MOE AcRF) Tier 1 Project (WBS: A-0009184-01-00).

Data Availability Statement: Data will be made available on request.

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

References

- 1. Kim, J.; Sengodan, S.; Kim, S.; Kwon, O.; Bu, Y.; Kim, G. Proton conducting oxides: A review of materials and applications for renewable energy conversion and storage. *Renew. Sust. Energ. Rev.* 2019, 109, 606–618. [CrossRef]
- 2. Xu, H.; Cao, M.; Li, Z.; Li, W.; Meng, S.; Song, H. Production of low carbon number olefins from natural gas: Methane-involved catalytic non-oxidative propane dehydrogenation. *Chem. Eng. J.* **2023**, *454*, 140508. [CrossRef]
- Olabi, A.G.; Abdelkareem, M.A.; Al-Murisi, M.; Shehata, N.; Alami, A.H.; Radwan, A.; Wilberforce, T.; Chae, K.-J.; Sayed, E.T. Recent progress in Green Ammonia: Production, applications, assessment, barriers, and its role in achieving the sustainable development goals. *Energy Convers. Manag.* 2023, 277, 116594. [CrossRef]
- 4. Suo, Y.; Yao, Y.; Zhang, Y.; Xing, S.; Yuan, Z.-Y. Recent advances in cobalt-based Fischer-Tropsch synthesis catalysts. *J. Ind. Eng. Chem.* **2022**, *115*, 92–119. [CrossRef]
- 5. Minette, F.; De Wilde, J. Multi-scale modeling and simulation of low-pressure methane bi-reforming using structured catalytic reactors. *Chem. Eng. J.* 2021, 407, 127218. [CrossRef]
- Kumar, N.; Shojaee, M.; Spivey, J.J. Catalytic bi-reforming of methane: From greenhouse gases to syngas. *Curr. Opin. Chem. Eng.* 2015, 9, 8–15. [CrossRef]
- Khademi, M.H.; Alipour-Dehkordi, A.; Tabesh, M. Optimal design of methane tri-reforming reactor to produce proper syngas for Fischer-Tropsch and methanol synthesis processes: A comparative analysis between different side-feeding strategies. *Int. J. Hydrogen Energy* 2021, 46, 14441–14454. [CrossRef]
- 8. Izquierdo, U.; Barrio, V.L.; Requies, J.; Cambra, J.F.; Güemez, M.B.; Arias, P.L. Tri-reforming: A new biogas process for synthesis gas and hydrogen production. *Int. J. Hydrogen Energy* **2013**, *38*, 7623–7631. [CrossRef]
- 9. Majewski, A.J.; Wood, J. Tri-reforming of methane over Ni@SiO2 catalyst. Int. J. Hydrogen Energy 2014, 39, 12578–12585. [CrossRef]
- Alipour-Dehkordi, A.; Khademi, M.H. Use of a micro-porous membrane multi-tubular fixed-bed reactor for tri-reforming of methane to syngas: CO₂, H₂O or O₂ side-feeding. *Int. J. Hydrogen Energy* 2019, 44, 32066–32079. [CrossRef]
- 11. Krenzke, P.T.; Fosheim, J.R.; Zheng, J.; Davidson, J.H. Synthesis gas production via the solar partial oxidation of methane-ceria redox cycle: Conversion, selectivity, and efficiency. *Int. J. Hydrogen Energy* **2016**, *41*, 12799–12811. [CrossRef]
- Zhang, S.; Li, T.; Wang, B.; Zhou, Z.; Meng, X.; Yang, N.; Zhu, X.; Liu, S. Coupling water splitting and partial oxidation of methane (POM) in Ag modified La_{0.8}Ca_{0.2}Fe_{0.94}O_{3-δ} hollow fiber membrane reactors for co-production of H₂ and syngas. *J. Membr. Sci.* 2022, 659, 120772. [CrossRef]
- 13. Gallucci, F.; Fernandez, E.; Corengia, P.; van Sint Annaland, M. Recent advances on membranes and membrane reactors for hydrogen production. *Chem. Eng. Sci.* 2013, 92, 40–66. [CrossRef]
- 14. Wang, H.; Wang, X.; Meng, B.; Tan, X.; Loh, K.S.; Sunarso, J.; Liu, S. Perovskite-based mixed protonic–electronic conducting membranes for hydrogen separation: Recent status and advances. *J. Ind. Eng. Chem.* **2018**, *60*, 297–306. [CrossRef]
- 15. Bernardo, G.; Araújo, T.; da Silva Lopes, T.; Sousa, J.; Mendes, A. Recent advances in membrane technologies for hydrogen purification. *Int. J. Hydrogen Energy* **2020**, *45*, 7313–7338. [CrossRef]
- 16. Deibert, W.; Ivanova, M.E.; Baumann, S.; Guillon, O.; Meulenberg, W.A. Ion-conducting ceramic membrane reactors for high-temperature applications. *J. Membr. Sci.* 2017, 543, 79–97. [CrossRef]
- 17. Hashim, S.S.; Somalu, M.R.; Loh, K.S.; Liu, S.; Zhou, W.; Sunarso, J. Perovskite-based proton conducting membranes for hydrogen separation: A review. *Int. J. Hydrogen Energy* **2018**, *43*, 15281–15305. [CrossRef]
- 18. Ye, K.; Li, K.; Lu, Y.; Guo, Z.; Ni, N.; Liu, H.; Huang, Y.; Ji, H.; Wang, P. An overview of advanced methods for the characterization of oxygen vacancies in materials. *TrAC Trends Anal. Chem.* **2019**, *116*, 102–108. [CrossRef]
- 19. Mather, G.C.; García-Martín, S.; Benne, D.; Ritter, C.; Amador, U. A-site-cation deficiency in the SrCe_{0.9}Yb_{0.1}O_{3-δ} perovskite: Effects of charge-compensation mechanism on structure and proton conductivity. *J. Mater. Chem.* **2011**, *21*, 5764–5773. [CrossRef]
- Tan, X.; Tan, X.; Yang, N.; Meng, B.; Zhang, K.; Liu, S. High performance BaCe_{0.8}Y_{0.2}O_{3-a} (BCY) hollow fibre membranes for hydrogen permeation. *Ceram. Int.* 2014, 40, 3131–3138. [CrossRef]
- Zhuang, L.; Li, J.; Xue, J.; Jiang, Z.; Wang, H. Evaluation of hydrogen separation performance of Ni-BaCe_{0.85}Fe_{0.15}O_{3-δ} cermet membranes. *Ceram. Int.* 2019, 45, 10120–10125. [CrossRef]
- 22. Ma, X.; Yang, C.; Chen, H.; Lv, Q.; Sun, K.; Li, W. Hydrogen permeation and chemical stability of Ni–BaCe_{0.7}In_{0.2}Ta_{0.1}O_{3-δ} cermet membrane. *Sep. Purif. Technol.* **2020**, 236, 116276. [CrossRef]
- Itagaki, Y.; Hiraoka, A.; Aono, H.; Yahiro, H. Hydrogen permeation of BaCe_{0.80}Y_{0.20}O_{3-δ}-Gd_{0.1}Ce_{0.9}O_x dual-phase membranes. J. Ceram. Soc. Jpn. 2017, 125, 338–342. [CrossRef]

- Yang, C.; Ma, X.; Chen, H.; Lv, Q.; Sun, K.; Chen, J.; Yun, S. Chemical stability and hydrogen permeation performance of Ni–BaCe_{0.7}Y_{0.3–X}InO_{3–δ} cermet membranes. *J. Alloys Compd.* 2018, 762, 409–414. [CrossRef]
- Polfus, J.M.; Xing, W.; Fontaine, M.-L.; Denonville, C.; Henriksen, P.P.; Bredesen, R. Hydrogen separation membranes based on dense ceramic composites in the La₂₇W₅O_{55.5}–LaCrO₃ system. *J. Membr. Sci.* 2015, 479, 39–45. [CrossRef]
- Jia, L.; Liu, M.; Xu, X.; Dong, W.; Jiang, H. Gd-doped ceria enhanced triple-conducting membrane for efficient hydrogen separation. Sep. Purif. Technol. 2021, 256, 117798. [CrossRef]
- Zhu, Z.; Hou, J.; He, W.; Liu, W. High-performance Ba(Zr_{0.1}Ce_{0.7}Y_{0.2})O_{3-δ} asymmetrical ceramic membrane with external short circuit for hydrogen separation. *J. Alloys Compd.* 2016, 660, 231–234. [CrossRef]
- Zhang, K.; Sunarso, J.; Pham, G.H.; Wang, S.; Liu, S. External short circuit-assisted proton conducting ceramic membrane for H₂ permeation. *Ceram. Int.* 2014, 40, 791–797. [CrossRef]
- Cheng, H.; Meng, B.; Li, C.; Wang, X.; Meng, X.; Sunarso, J.; Tan, X.; Liu, S. Single-step synthesized dual-layer hollow fiber membrane reactor for on-site hydrogen production through ammonia decomposition. *Int. J. Hydrogen Energy* 2020, 45, 7423–7432. [CrossRef]
- Mercadelli, E.; Gondolini, A.; Montaleone, D.; Pinasco, P.; Escolástico, S.; Serra, J.M.; Sanson, A. Production strategies of asymmetric BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-δ}—Ce_{0.8}Gd_{0.2}O_{2-δ} membrane for hydrogen separation. *Int. J. Hydrogen Energy* 2020, 45, 7468–7478. [CrossRef]
- Meng, B.; Wang, H.; Cheng, H.; Wang, X.; Meng, X.; Sunarso, J.; Tan, X.; Liu, S. Hydrogen permeation performance of dual-phase protonic-electronic conducting ceramic membrane with regular and independent transport channels. *Sep. Purif. Technol.* 2019, 213, 515–523. [CrossRef]
- 32. Meng, X.; Shang, Y.; Meng, B.; Yang, N.; Tan, X.; Sunarso, J.; Liu, S. Bi-functional performances of BaCe_{0.95}Tb_{0.05}O_{3-δ}-based hollow fiber membranes for power generation and hydrogen permeation. *J. Eur. Ceram. Soc.* **2016**, *36*, 4123–4129. [CrossRef]
- Wang, T.; Wang, H.; Meng, X.; Meng, B.; Tan, X.; Sunarso, J.; Liu, S. Enhanced hydrogen permeability and reverse water–gas shift reaction activity via magneli Ti₄O₇ doping into SrCe_{0.9}Y_{0.1}O_{3-δ} hollow fiber membrane. *Int. J. Hydrogen Energy* 2017, 42, 12301–12309. [CrossRef]
- 34. Wu, Z.; Wang, B.; Li, K. A novel dual-layer ceramic hollow fibre membrane reactor for methane conversion. *J. Membr. Sci.* 2010, 352, 63–70. [CrossRef]
- 35. Shi, Y.; Wang, J.; Li, C.; Song, J.; Meng, B.; Sunarso, J.; Meng, X.; Yang, N.; Tan, X.; Liu, S. High flux and CO₂ stable La_{0.6}Ca_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} hollow fiber membranes through internal coagulation bath optimization. *J. Eur. Ceram. Soc.* 2023, 43, 5575–5586. [CrossRef]
- Meng, B.; Wu, S.; Zhang, S.; Li, C.; Song, J.; Yang, N.; Sunarso, J.; Tan, X.; Wang, M.; Liu, S. CO₂-stable and cobalt-free Ce_{0.8}Sm_{0.2}O_{2-δ}-La_{0.8}Ca_{0.2}Al_{0.3}Fe_{0.7}O_{3-δ} dual-phase hollow fiber membranes for oxygen separation. *Sep. Purif. Technol.* 2022, 300, 121900. [CrossRef]
- Song, J.; Wang, Z.; Tan, X.; Cui, Y.; Kawi, S.; Liu, S. Simultaneous hydrogen and oxygen permeation through BaCe_{0.70}Fe_{0.10}Sc_{0.20}O_{3-δ} perovskite hollow fiber membranes. *J. Membr. Sci.* 2021, 635, 119513. [CrossRef]
- Song, J.; Feng, B.; Tan, X.; Han, N.; Sunarso, J.; Liu, S. Oxygen selective perovskite hollow fiber membrane bundles. J. Membr. Sci. 2019, 581, 393–400. [CrossRef]
- Rosensteel, W.A.; Ricote, S.; Sullivan, N.P. Hydrogen permeation through dense BaCe_{0.8}Y_{0.2}O_{3-δ}-Ce_{0.8}Y_{0.2}O_{2-δ} compositeceramic hydrogen separation membranes. *Int. J. Hydrogen Energy* 2016, 41, 2598–2606. [CrossRef]
- Tan, X.; Shen, Z.; Bokhari, A.; Ali, W.; Han, N. Effect of Co₂O₃ as sintering aid on perovskite BaCe_{0.8}Y_{0.2}O_{3-δ} proton conductive membrane for hydrogen separation. *Int. J. Hydrogen Energy* 2023, *48*, 26551–26558. [CrossRef]
- Leng, Z.; Huang, Z.; Zhou, X.; Zhang, B.; Bai, H.; Zhou, J.; Wang, S. The effect of sintering aids on BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-δ} as the electrolyte of proton-conducting solid oxide electrolysis cells. *Int. J. Hydrogen Energy* **2022**, 47, 33861–33871. [CrossRef]
- Jia, L.; Ashtiani, S.; Liang, F.; He, G.; Jiang, H. Hydrogen permeation through dual-phase ceramic membrane derived from automatic phase-separation of SrCe_{0.50}Fe_{0.50}O_{3-δ} precursor. *Int. J. Hydrogen Energy* **2020**, 45, 4625–4634. [CrossRef]
- 43. Unemoto, A.; Kaimai, A.; Sato, K.; Yashiro, K.; Matsumoto, H.; Mizusaki, J.; Amezawa, K.; Kawada, T. Hydrogen permeability and electrical properties in oxide composites☆. *Solid State Ion.* **2008**, *178*, 1663–1667. [CrossRef]
- Rebollo, E.; Mortalo, C.; Escolastico, S.; Boldrini, S.; Barison, S.; Serra, J.M.; Fabrizio, M. Exceptional hydrogen permeation of all-ceramic composite robust membranes based on BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-δ} and Y- or Gd-doped ceria. *Energ. Environ. Sci.* 2015, *8*, 3675–3686. [CrossRef]
- Ivanova, M.E.; Escolástico, S.; Balaguer, M.; Palisaitis, J.; Sohn, Y.J.; Meulenberg, W.A.; Guillon, O.; Mayer, J.; Serra, J.M. Hydrogen separation through tailored dual phase membranes with nominal composition BaCe_{0.8}Eu_{0.2}O_{3-δ}:Ce_{0.8}Y_{0.2}O_{2-δ} at intermediate temperatures. *Sci. Rep.* 2016, *6*, 34773. [CrossRef] [PubMed]
- Cheng, S.; Wang, Y.; Zhuang, L.; Xue, J.; Wei, Y.; Feldhoff, A.; Caro, J.; Wang, H. A dual-phase ceramic membrane with extremely high H₂ permeation flux prepared by autoseparation of a ceramic precursor. *Angew. Chem. Int. Ed.* 2016, 55, 10895–10898. [CrossRef]

- 47. Fish, J.S.; Ricote, S.; O'Hayre, R.; Bonanos, N. Electrical properties and flux performance of composite ceramic hydrogen separation membranes. *J. Mater. Chem. A* 2015, *3*, 5392–5401. [CrossRef]
- Escolástico, S.; Solís, C.; Kjølseth, C.; Serra, J.M. Outstanding hydrogen permeation through CO₂-stable dual-phase ceramic membranes. *Energy Environ. Sci.* 2014, 7, 3736–3746. [CrossRef]

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