Relationship between fabrication method and chemical stability of Ni–
 $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ membrane

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Abstract: NiO effectively promotes the sintering of highly refractory Y-doped BaZrO₃ (BZY) through the formation of BaY₂NiO₅, providing a simple and cost-effective method for the fabrication of dense BZY electrolyte and Ni–BZY hydrogen separation membrane at ~1400 °C. Unfortunately, insulating BaCO₃ and Y₂O₃ phases formed on the surface of BZY and Ni–BZY prepared by solid state reaction method with NiO after annealing in wet CO₂. Ni–BZY membranes prepared from different methods suffered different degree of performance loss in wet H₂ at 900 °C. The chemical instability of Ni–BZY is attributed to the formation of a secondary phase (BaY₂O₄) generated from the reduction of BaY₂NiO₅ in H₂ during the sintering process. Both BaY₂O₄ and BaY₂NiO₅ react with H₂O, and CO₂ at elevated temperatures, generating insulating Ba(OH)₂ and BaCO₃ phases, respectively. The less BaY₂O₄ is formed in the fabrication process, the better chemical stability the Ni–BZY membranes possess. Therefore, a new Ni–BZY membrane is prepared through a judicious combination of BZY powders prepared from combined EDTA-citric and solid state reaction methods, and demonstrates exceptional chemical stability in H₂O and CO₂, enabling stable and even improved hydrogen flux in wet 50% CO₂ at 900 °C.

Keywords: hydrogen permeation; composite membrane; high temperature proton conductor; barium zirconate; chemical stability.

1. Introduction

Hydrogen separation membranes based on high temperature proton conductors have been pursued for a long time because of its potential to greatly reduce the energy and capital cost of large-scale hydrogen production from steam methane reforming (SMR) [1-4]. A key to their successful applications is the development of a membrane with high performance, chemical and mechanical stability. Yttrium-doped barium cerate (BCY) possesses high proton conductivity but poor chemical stability in H_2O and CO_2 [5-7]. Numerous efforts have been devoted to the improvement of its chemical stability, mainly through the partial replacement of Ce by cations such as In, Sn, Ti, Zr, Nb, Ta, etc [2,8-12]. The performance of Ni-BaCe_{0.8}Y_{0.2}O_{3- δ} (Ni-BCY) and Ni-BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3- δ} (Ni-BZCY) degraded ~100% and 43%, respectively, in wet 40% H_2 and 30% CO_2 at 900 °C [2]. Recently, Yang *et al.* discovered that the introduction of Yb simultaneously improved the proton conductivity and chemical stability of BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3- δ} [13]. Therefore, Ni-BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3- δ} (Ni-BZCYYb) membrane was developed and showed outstanding performance [3,4]. Ni-BZCYYb membrane presented stable and greatly improved performance when CO_2 was introduced into dry H_2 due to the increase of moisture content caused by the reverse water gas shift (RWGS) reaction [4]. Unfortunately, further study showed that the reaction between BZCYYb and CO_2 was promoted by high content of H_2O , therefore, Ni-BZCYYb membrane also suffered performance degradation in wet 40% H_2 and 30% CO_2 at 900 °C (11.4%, less than that of Ni-BCY and Ni-BZCY) [14].

Another strategy is to develop hydrogen separation membranes with chemically stable proton conductors such as Ln₆WO_{12- δ} (Ln refers to lanthanides), Ca-doped LaNbO₄, and Ni-La_{0.4875}Ca_{0.0125}Ce_{0.5}O_{2- δ} , but their performances are still much inferior to that of Ni-BZCYYb, mostly due to their lower proton and/or electronic conductivities [15-20]. Y-doped BaZrO₃

(BZY) has recently been explored as a proton conductor for electrolyte of solid oxide fuel cells and hydrogen separation membranes because of its excellent bulk proton conductivity and chemical stability [19,21-27]. Since $\text{BaZr}_{0.8}\text{Y}_{0.15}\text{Mn}_{0.15}\text{O}_{3-\delta}$ (BZYM) shows very poor hydrogen flux due to the lack of electronic conductivity [19], dense composite Ni–BZY membranes have been fabricated and demonstrated much higher hydrogen flux than that of BZYM [27]. During the fabrication of BZY and Ni–BZY membranes, the main obstacles are BZY’s highly refractory nature, poor grain boundary proton conductivity, and high number of grain boundaries due to limited grain growth during sintering [21,28-31]. One viable solution to these problems is the adoption of sintering aids (e.g., NiO, ZnO, CuO, LiNO_3) which can significantly lower the sintering temperature of BZY and promote the grain growth [32-41]. NiO has been reported as the most effective sintering aid in promoting the grain growth, which is crucial to reduce the large grain boundary resistance [37,38]. Dense BZY ceramic with grains as large as 5 μm can be achieved using BZY powders prepared by solid state reactive sintering method with 1 wt.% NiO after sintering at 1500 $^{\circ}\text{C}$ for 24 h, accompanied by the formation of a secondary phase, BaY_2NiO_5 , which has a low melting point and promotes the sintering of BZY [38]. In our previous study, dense Ni–BZY membrane with large BZY grains (1~2 μm) was successfully fabricated using BZY powder prepared by solid state reaction method with 2 wt.% NiO (denoted as BZYNiO2) containing BaY_2NiO_5 [27]. In contrast, the BZY grains are very small (~0.25 μm) in the membrane prepared using Ni–BZY powder obtained from the gel combustion method and subsequent reduction, which contains no BaY_2NiO_5 [27]. Apparently, BaY_2NiO_5 plays an important role in the fabrication of dense Ni–BZY membrane with large BZY grains.

These studies have mainly focused on the sintering behavior, microstructure, and electrical/permeation properties. No work has been reported on the chemical stability of BZY

and Ni-BZY in H_2 , H_2O , and CO_2 after the introduction of the sintering aids, which is crucial for their successful applications. Although the weight ratio of NiO sintering aid seems to be low, the weight ratio of BaY_2NiO_5 is high due to the large difference in molecular weight between BaY_2NiO_5 ($453.83 \text{ g mol}^{-1}$) and NiO (74.69 g mol^{-1}). If 2 wt.% NiO (based on the total weight of $BaCO_3$, ZrO_2 , and Y_2O_3) is completely converted to BaY_2NiO_5 , there should be 13.8 wt.% BaY_2NiO_5 in the BZYNiO2 ceramic. Unlike BZY, BaY_2NiO_5 may be unstable in H_2 , H_2O , or CO_2 -containing atmospheres at elevated temperatures, potentially leading to the chemical instability of BZYNiO2 ceramic and Ni-BZY membrane, and thus insulating phases will be formed on the surfaces and the performance will degrade after exposure to H_2O and CO_2 . Fortunately, this problem can be mitigated by reducing the amount of BaY_2NiO_5 through tailoring the BZY powders used in the fabrication process. In the Ni-BZY membrane prepared with BZYNiO2 (denoted as Ni-BZY1), 2 wt.% NiO was directly mixed with $BaCO_3$, Y_2O_3 , and ZrO_2 in the preparation of BZYNiO2. A lot of BaY_2NiO_5 is formed in the following calcination process. Ni-BZY2 membrane is fabricated using $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ prepared by solid state reaction method without NiO (denoted as BZY20-SSR). However, BaY_2NiO_5 is still formed by the reaction among NiO (formed by partial oxidation of Ni during the sintering in N_2 containing a little oxygen), residual $BaCO_3$, and Y_2O_3 in BZY20-SSR [27]. Because the amount of $BaCO_3$ and Y_2O_3 is much less than that in uncalined BZYNiO2, the amount of BaY_2NiO_5 in Ni-BZY2 should be less than that of Ni-BZY1. In order to further reduce the amount of BaY_2NiO_5 , we employee BZY20 powder prepared by combined EDTA-citric (CEC) method (BZY20-CEC). CEC is a wet-chemical method and the distribution of particles is much more homogeneous than that of solid state reaction. Therefore, BZY20-CEC is free of residual $BaCO_3$ and Y_2O_3 after calcination, and will not contribute to the formation of BaY_2NiO_5 , which allows us to adjust the

amount of BaY_2NiO_5 by partially replacing BZY20-SSR with BZY-CEC. Therefore, another two Ni-BZY membranes were prepared by further replacing 60% and 80% BZY20-SSR powder in Ni-BZY2 by BZY20-CEC (denoted as Ni-BZY3 and Ni-BZY4, respectively). The amount of BaY_2NiO_5 is expected to follow this order: Ni-BZY1>Ni-BZY2>Ni-BZY3>Ni-BZY4.

In this study, the performance stability of these Ni-BZY membranes was evaluated in wet H_2 with and without CO_2 at 900 °C. The chemical stability of BaY_2NiO_5 , BZYNiO2, and Ni-BZY was investigated in H_2 , H_2O , and CO_2 -containing atmospheres. A stable Ni-BZY membrane was developed, demonstrating excellent chemical and performance stability in the presence of H_2 , H_2O , and CO_2 .

2. Experimental

Fig. 1 shows the schematic of the material synthesis and chemical stability test processes employed in this work. All chemicals were purchased from Alfa Aesar with purity>99.5%. BZY powders were prepared through the solid state reaction method using 0 and 2 wt.% NiO as sintering aid (denoted as BZY20 and BZYNiO2, respectively). For simplicity, only BZYNiO2 is shown in Fig. 1. Stoichiometric amounts of BaCO_3 , ZrO_2 , and Y_2O_3 were ball-milled in ethanol with ZrO_2 balls for 24 h. 0 and 2 wt.% NiO based on the total weight of BaCO_3 , ZrO_2 , and Y_2O_3 were added to the powder mixture prior to the ball-milling to obtain BZY20 and BZYNiO2 powders, respectively. The ball-milled powders were dried and then pressed into pellets followed by calcination at 1300 °C for 10 h. The calcined pellets were milled to obtain BZY20 and BZYNiO2 powders, respectively. To obtain dense BZYNiO2 ceramic, calcined and milled BZYNiO2 powders were pressed into pellets and then sintered at 1500 °C for 10 h in air. Some

BZY20 powder was also prepared by the combined EDTA-citric acid (CEC) method and calcined at 1100 °C for 10 h (denoted as BZY20-CEC) [27].

To study the effect of phase composition on the chemical stability of Ni–BZY membranes, different BZY powders with different weight contents were used to fabricate 4 different Ni–BZY membranes (as listed in Table 1). Calculated amounts of BZYNiO₂, BZY20, and BZY20-CEC powders were mixed with Ni powders in volume ratio of 60:40 (ceramic vs Ni). These powders were ball-milled, dried, milled, and pressed into pellets with a 20-mm stainless steel die under the pressure of 100 MPa. These pellets were sintered at 1440 °C for 20 h in N₂ and another 20 h in 5% H₂/N₂. During the sintering process in N₂ (contains ~0.02 vol.% O₂, measured by gas chromatography), partial Ni was oxidized to NiO which reacted with residual BaCO₃ and Y₂O₃, forming BaY₂NiO₅ and promoting the densification and grain growth of BZY phase [27]. During the sintering process in 5% H₂/N₂, residual NiO was reduced to Ni and BaY₂NiO₅ decomposed forming Ni and a secondary phase. The reduction was confirmed by the increase of water content from ~0.3% to ~2.4% in the gas after switching N₂ to 5% H₂/N₂, monitored by a humidity sensor (Vaisala HMT338). The extended sintering time in 5% H₂/N₂ allowed the elimination of pores generated by the decomposition of BaY₂NiO₅.

The sintered BZYNiO₂, Ni–BZY pellets were polished on a Bluehler polisher with SiC sandpapers (320, 600, 1200 grits) and then diamond dispersion solution (9, 3, 1 μm) to reveal the surface microstructure. Polished BZYNiO₂ pellet was annealed in wet CO₂ (3% H₂O) at 700 °C for 100 h to study its chemical stability in CO₂. A polished Ni–BZY1 sample was thermally etched at 1300 °C for 30 min in 5% H₂/N₂ for surface microstructure study. To test the chemical stability in water, the polished Ni–BZY pellets (~1 g in weight) were boiled in 30 mL deionized water for 20 h in Teflon-lined stainless steel autoclaves. The polished Ni–BZY samples were

also annealed in a gas mixture containing 3 vol% H₂O, 17 vol% H₂ and 80 vol% CO₂ at 900 °C for 50 h to test the chemical stability in wet CO₂. Details for the hydrogen flux measurements can be found in our previous report [4].

BaY₂NiO₅ was synthesized by the solid state reaction (SSR) method. Stoichiometric amounts of BaCO₃, Y₂O₃, and NiO powders were ball-milled for 24 h in ethanol with ZrO₂ balls for 24 h. The powders were dried, pressed into pellets, and calcined at 1300 °C for 10 h. The pellets were milled into powders and then annealed in either dry/wet H₂ at 900 °C for 20 h, or wet CO₂ at 900 °C for 10 h.

X-ray diffraction (XRD, Rigaku D/Max 2100, with Cu K α radiation) analysis was used to identify the phases present in the powders and pellets. Rietveld refinements were carried out with GSAS package [42]. Field emission scanning electronic microscopy (FESEM, Zeiss ultra plus) equipped with Energy-dispersive X-ray spectroscopy (EDX, Oxford) was used to study the microstructure and composition of the BZY and Ni-BZY membranes.

3. Results and discussion

3.1 Performance stability in wet H₂

Fig. 2 shows the time dependence of hydrogen flux of various Ni-BZY membranes at 900 °C in wet 20% H₂ (containing 3 vol% H₂O). The initial performance of the membranes follows such an order: Ni-BZY1>Ni-BZY3>Ni-BZY4 (3.6, 2.8, and 2.0*10⁻⁸ mol/cm²s, respectively). In order to find the reason for the different initial flux, we investigated the microstructure of the membranes. Fig. S1 shows the cross-sectional SEM images of these membranes. All membranes are composed of large Ni grains and small BZY grains. The grain sizes of BZY are estimated to be 1.44, 1.17, and 0.78 μ m for Ni-BZY1, Ni-BZY3, and Ni-BZY4, respectively (see calculation details in caption of Fig. S1). Similar trend is observed for the permeation flux and grain size of

BZY in Ni-BZY membranes. It is well-known that BZY possesses high bulk proton conductivity but suffers from poor grain boundary proton conductivity [43]. Therefore, BZY ceramic with larger grain size and fewer grain boundaries also shows larger total proton conductivity than that with small grain size [21,22]. Since the Ni-BZY membranes show the same behavior with BZY ceramics, the higher initial flux of Ni-BZY membranes with larger BZY grains is attributed to their fewer grain boundaries and higher total proton conductivities. The difference in grain sizes is due to the difference in the amount of BaY_2NiO_5 formed during the sintering process in N_2 , and BaY_2NiO_5 promotes the grain growth of BZY phase.

The flux of Ni-BZY1 first degrades quickly and then slowly, with a total flux loss of 21.5% in 180 h. The flux of Ni-BZY3 degrades 15.0% in 200 h. However, the flux of Ni-BZY4 keeps stable during the whole test process (~160 h). It seems that there is a trade-off between the initial flux and performance stability of these membranes. Since both Ni and BZY are thermodynamically stable in H_2 and H_2O , it's hard to explain the degradation behavior. Therefore, we investigated the phase composition and microstructure of Ni-BZY1 membrane after the permeation test. Fig. S2 shows the XRD patterns obtained from fresh, feed, and sweep side surfaces of Ni-BZY1 membrane. Unlike the fresh membrane which only consists of Ni and BZY, the tested feed and sweep side surfaces contain much less BZY. Both BaCO_3 and YOOH are found on the feed and sweep side surfaces. The SEM images in Fig. S3 show that the feed side surface is completely covered by new phases with plate-like structure, while the sweep side surface is only partially covered. EDX results in Fig. S4 show that the plate-like phases contain Ba, C, Y, and O, indicating that they are BaCO_3 and YOOH , as revealed by the XRD results. Since the feed gas is wet H_2 without CO_2 , BaCO_3 is formed by reaction between Ba(OH)_2 and CO_2 in air after the permeation test. These insulating phases (Ba(OH)_2 and YOOH) can block the

pathways for hydrogen permeation, which explains the degradation behavior, but the sources of these insulating phases are still unclear. To obtain more insight in the sources of Ba(OH)_2 and YOOH , we investigated the chemical stability of Ni-BZY membranes by treating them in boiling water for 20 h or wet 17 vol% H_2 and 80 vol% CO_2 at 900 °C for 50 h.

3.2 Chemical stability in boiling water and wet CO_2

Fig. 3a-d shows the SEM images obtained from polished surface of fresh Ni-BZY1, 2, 3, and 4 membranes. The dark and grey phases are Ni and BZY, respectively. Many small ($\sim 3 \mu\text{m}$) bumps (indicated by red arrows) are found on the surface of Ni-BZY1. SEM-EDX analysis of polished Ni-BZY1 membrane (Fig. S5) show that these bumps contain Ba, C, and Y, but no Ni, which can be BaCO_3 and Y_2O_3 . Fig. S6 shows the SEM-EDX results of the polished and thermally etched Ni-BZY1 membrane. The bumps found in Fig. S5 disappeared, but some clusters formed by fine nanoparticles are found. EDX mapping results show that the porous clusters are rich in Y but are depleted of Ba, indicating that these clusters are Y_2O_3 . This can be explained by the decomposition of BaCO_3 at 1300 °C forming volatile BaO, which evaporates to the atmosphere and leaves Y_2O_3 behind. These results suggest that the secondary phases formed in the fabrication process are ready to react with $\text{H}_2\text{O}/\text{CO}_2$ in air even at room temperature, forming BaCO_3 and Y_2O_3 , which grow out of the polished surface. Unlike the small bumps found in Ni-BZY1, a few large ($\sim 20 \mu\text{m}$) bumps with cracks are found on the surface of Ni-BZY2. There are much fewer bumps on the surface of Ni-BZY3, and it's difficult to find the bumps on the surface of Ni-BZY4. Therefore, the number of bumps and the amount of secondary phases follow such an order: Ni-BZY1>Ni-BZY2>Ni-BZY3>Ni-BZY4.

Fig. 4a shows the XRD pattern obtained from surface of Ni-BZY1 after treatment in boiling water for 20 h (Similar results are also obtained for Ni-BZY2, 3, and 4). Only peaks of Ni and

BZY are present in both patterns, confirming that the Ni and BZY phases are stable in boiling water. However, the pH value of the deionized water used in the boiling test for Ni-BZY1 and Ni-BZY2 increased from 7 to 12. Precipitate was observed after H_2SO_4 was added to the water, indicating formation of BaSO_4 (the sulphates of Ni, Y, Zr were all soluble in water). These results suggested that Ba(OH)_2 was formed during the boiling of the membranes. Because Ba(OH)_2 was soluble in water and the polished surface was very smooth, its amount on the membrane surface was too low to be detected by XRD. On the other hand, the pH value of water for boiling Ni-BZY3 and Ni-BZY4 kept at ~ 8 , suggesting very small amount of Ba(OH)_2 was formed during the boiling process. After boiling test, significant microstructure damage is observed on the surfaces of Ni-BZY1 and Ni-BZY2 membranes. The characteristics of the surface microstructure damage agree very well with the sizes and distribution of secondary phases, such as small dotted bumps in boiled Ni-BZY1 (Fig. 3e) and small dotted bumps in polished Ni-BZY1 (Fig. 3a), large cracks in boiled Ni-BZY2 (Fig. 3f) and large bumps in polished Ni-BZY2 (Fig. 3b). A close look at the small bumps on boiled surface of Ni-BZY1 shows that they consist of BZY grains in the bottom and Y_2O_3 on the top (Fig. 3e, zoomed-in view in Fig. S7a with EDX spectrum in Fig. S7c). In contrast, Ni-BZY3 and Ni-BZY4 show no cracks or bumps. These results suggest the secondary phases in Ni-BZY1 react with H_2O forming a lot of Ba(OH)_2 and Y_2O_3 , which can explain the formation of insulating phases on the membrane surfaces and thus the performance degradation in wet H_2 .

XRD patterns in Fig. 4b-d show that a significant amount of BaCO_3 is detected on Ni-BZY1 and less is found on Ni-BZY2 after annealing in wet 80% CO_2 . Surprisingly, no BaCO_3 is found on Ni-BZY3 and Ni-BZY4. This is further verified by SEM images in Fig. 3i-l. Most of the surfaces of Ni-BZY1 and Ni-BZY2 membranes are covered by the new phases. EDX spectrum

shows that the new phases on Ni-BZY1 is composed of Ba, C, and O (part of Fig. 3i magnified in Fig. S7b coupled with EDX spectrum in Fig. S7d), which also suggests that the new phases is BaCO_3 . However, there are only a little BaCO_3 on Ni-BZY3 (indicated by arrows in Fig. 3k), which is below the detection limit of XRD. For Ni-BZY4, no BaCO_3 is observed. The amount of BaCO_3 follow such order: Ni-BZY1>Ni-BZY2>Ni-BZY3>Ni-BZY4. It is noticeable that Ni-BZY4 shows excellent chemical stability in both boiling water and wet CO_2 .

3.3 Mechanism study of performance degradation and chemical instability

Fig. S2-4 suggest that the performance degradation of Ni-BZY1 in wet H_2 is caused by the blocking phases (Ba(OH)_2 and YOOH) formed on the membrane surfaces. The chemical stability study shows that Ba(OH)_2 and Y_2O_3 is formed by the reaction between the secondary phases and water. Therefore, the flux degradation in wet H_2 is caused by Ba(OH)_2 and YOOH generated from the reaction between the secondary phase and H_2O . The more secondary phases there are in Ni-BZY membranes, the more $\text{Ba(OH)}_2+\text{Y}_2\text{O}_3$ is formed when exposed to water, and the more the performance degrades. The question is what the secondary phases are and where they come from. In the previous study, we observed BaY_2NiO_5 after Ni-BZY membranes were sintered in N_2 only. After the second sintering process in 5% H_2/N_2 , BaY_2NiO_5 disappeared but no new phase was found by XRD [27]. It is difficult to identify the new phases directly because they are mixed with large amount of Ni and BZY and are ready to react with $\text{H}_2\text{O}/\text{CO}_2$ in air as seen from Fig. 3a-b. Therefore, we prepared BaY_2NiO_5 separately and investigated its chemical stability under various conditions.

Fig. 5 shows the XRD patterns of BaY_2NiO_5 before and after annealing in different atmospheres at 900 °C. After calcination at 1300 °C for 10 h, Immm structured BaY_2NiO_5 with lattice parameters of $a=3.757 \text{ \AA}$, $b=5.754 \text{ \AA}$, and $c=11.315 \text{ \AA}$ is obtained (Fig. 5a, see Rietveld

refinement profile in Fig. S8). After annealing in CO₂ at 900 °C for 10 h (Fig. 5b), BaY₂NiO₅ powder decomposes into a mixture of BaCO₃, Y₂O₃, and NiO (BaY₂NiO₅+CO₂=BaCO₃+Y₂O₃+NiO). After annealing in dry H₂ (Fig. 5c), BaY₂NiO₅ decomposes into BaY₂O₄ and Ni (BaY₂NiO₅+H₂=BaY₂O₄+Ni+H₂O). After annealing in wet H₂ (Fig. 5d), aside from BaY₂O₄ and Ni, Y₂O₃ and BaCO₃ are found, suggesting that BaY₂O₄ partially reacts with H₂O forming Y₂O₃ and Ba(OH)₂ which is converted to BaCO₃ when exposed to air. These results indicate that BaY₂NiO₅ is unstable in H₂, H₂O, and CO₂-containing atmospheres at 900 °C, leading to the formation of insulating BaY₂O₄, Ba(OH)₂, and BaCO₃, respectively. Coors investigated reduced BaCe_{0.2}Zr_{0.6}Y_{0.2}O_{3-δ} (BCZY262, sintered with 1 wt.% NiO by solid state reactive sintering method) by field emission SEM and high resolution transmission electron microscopy (HRTEM) [44]. Only Ni metallic nanoprecipitates and some amorphous grain boundaries were observed. Therefore, BaY₂NiO₅ was assumed to decompose into Ni, BaO, and Y₂O₃ in reducing atmosphere. Then BaO and Y₂O₃ were dissolved back to perovskite lattice [44]. In that case, BZYNiO₂ should be chemically stable, which cannot explain the catastrophic failure of sintered BCZY262 ceramic during cooling below 400 °C in wet H₂ [44]. Instead, the failure can be attributed to the stress originated from volume increase accompanied with the reaction between BaY₂O₄ and H₂O forming Ba(OH)₂ and Y₂O₃. BaY₂O₄ can be prepared by calcination of BaCO₃ and Y₂O₃ at 1000 °C for 10 h [45], suggesting that BaY₂O₄ is more stable than BaO (from decomposition of BaCO₃) and Y₂O₃ at elevated temperature in H₂O/CO₂-free condition. Therefore, after sintering in N₂ and then 5% H₂, BaY₂NiO₅ in Ni–BZY decomposes into BaY₂O₄ and Ni, rather than BaO, Y₂O₃, and Ni. Unfortunately, both BaY₂O₄ and BaY₂NiO₅ easily react with H₂O and CO₂, forming insulating phases.

These results can provide a clear explanation on the performance and chemical instability found in Ni-BZY1, 2, and 3 membranes. In Ni-BZY1, BaY_2NiO_5 is formed during the fabrication of BZYNiO2 powder. In Ni-BZY2, 3, and 4, residual BaCO_3 and Y_2O_3 in BZY20 prepared by the SSR method reacts with NiO (from the oxidation of partial metal Ni in N_2 containing 0.02% O_2) forming BaY_2NiO_5 . BaY_2NiO_5 is reduced to BaY_2O_4 and Ni during sintering in 5% H_2/N_2 . BaY_2O_4 is distributed as isolated islands and react with H_2O during permeation test in H_2 , forming insulating barium and yttrium hydroxides on the membrane surfaces and causing the performance degradation. BaY_2O_4 reacts with H_2O and CO_2 forming $\text{Ba}(\text{OH})_2+\text{Y}_2\text{O}_3$ and $\text{BaCO}_3+\text{Y}_2\text{O}_3$ during the chemical stability test in boiling water and wet CO_2 , respectively. Less BaY_2O_4 will lead to less insulating phases on the membrane surfaces and less performance degradation when exposed to H_2O and CO_2 , as observed in the performance and chemical stability study. In Ni-BZY3 and Ni-BZY4, the BZY20-CEC grains also act as a covering layer for BaY_2O_4 , and keeps BaY_2O_4 away from attack by CO_2 and H_2O , leading to higher chemical stability. Similar strategy has been employed in a $\text{BaCe}_{0.8}\text{Sm}_{0.2}\text{O}_{3-\delta}$ - $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ composite electrolyte and successfully avoided the chemical instability issue of $\text{BaCeO}_{3-\delta}$ [46]. Apparently, the amount of BaY_2O_4 is too large to be fully covered by BZY20-CEC in Ni-BZY3, but is small enough to be fully covered by BZY20-CEC in Ni-BZY4. We also tried to prepare Ni-BZY membrane only with BZY20-CEC powder, however, the obtained membrane possessed significant porosity due to lack of BaY_2NiO_5 as sintering aid. The Ni-BZY4 membrane demonstrated both excellent chemical stability and sinteractivity, and its performance stability was further tested in wet CO_2 .

3.4 Performance and microstructural stability of Ni-BZY4 membrane in wet CO_2

Hydrogen separation membranes are expected to be applied in wet H₂ with considerable amount of CO₂. Therefore, its performance stability in CO₂ is critical to its application. Fig. 6 shows that the flux of Ni–BZY4 membrane in 40% H₂ increases from 2.5*10⁻⁸ to 2.8*10⁻⁸ and 2.9*10⁻⁸ mol/cm²s after introduction of 30% and 50% CO₂, respectively. Except for the initial flux increase, the flux keeps stable during the test in wet CO₂ for 225 h. The flux increase is ascribed to the reverse water gas shift (RWGS, H₂+CO₂→H₂O+CO) reaction which leads to the increase of moisture content in feed gas and thus proton conductivity in BZY phase, which is previously observed in Ni–BZCYYb membrane [4,14]. The RWGS reaction consumes equal amount of H₂ and CO₂, generating same amount of H₂O and CO. The measured CO content is 1.9% after the introduction of 30% CO₂, indicating that the moisture content increases from 3% (from the water bubbler) to 4.9%, and the hydrogen content decreases from 40% to 38.1%. The former is beneficial for the increase of the proton conductivity of BZY and hydrogen flux, while the latter is deleterious to hydrogen flux by reducing hydrogen partial pressure gradient across the membrane. Nevertheless, the flux increases, suggesting the former is dominant in the case of Ni–BZY4 membrane. In a very recent report, Zhu *et al.* developed a dense Ni–BaZr_{0.7}Pr_{0.1}Y_{0.2}O_{3-δ} (Ni–BZPY) membrane utilizing the benefit of Pr-doping on the sinter-activity of BZY [47]. Because Pr⁴⁺ can easily be reduced to Pr³⁺ and even Pr²⁺, the doping of Pr in BZY introduces additional oxygen vacancies, which can promote the RWGS reaction, as observed in Ce-doped BZY [48]. The hydrogen content in feed gas decreased dramatically from 40% to 28% after introduction of 30% CO₂ at 850 °C. Therefore, the flux decreased from 7.3*10⁻⁹ to 6.1*10⁻⁹ mol/cm²s. Besides, the flux of a 0.40-mm-thick Ni–BZPY membrane in wet 40% H₂ at 900 °C was only 9.2*10⁻⁹ mol/cm²s, much lower than that of Ni–BZY4 membrane (2.5*10⁻⁸

⁸ mol/cm²s in the same condition). Therefore, Ni-BZY4 is superior to Ni-BZPY membrane in both performance and performance stability.

After permeation test in wet CO₂, the microstructure of Ni-BZY4 membrane was investigated by SEM. Fig. 7a shows that the whole membrane is still compact and no obvious porosity is observed. There is no coarsening of Ni particles close to the feed side surface (Fig. 7a, b, and c). Only peaks of Ni and BZY can be found in the XRD pattern obtained from the feed side surface (Fig. S9). The feed side surface (Fig. 7b) consists of large Ni particles and small BZY grains. In comparison, the feed side surface of Ni-BZY1 membrane are completely covered by plate-like phases including BaCO₃ and YOOH after test in wet H₂, which is much milder than wet 50% CO₂ (Fig. S2-4). Although the surface looks porous, the cross-sectional view (Fig. 7c) shows the porous layer only reaches a depth of several microns. Similar microstructure is observed on the sweep side of the membrane (Fig. 7d).

Although Ni-BZCYYb membrane displays very high permeation flux [3,4], the long-term chemical and mechanical stability issues make it less attracting than Ni-BZY4 membrane. After a 0.56-mm-thick Ni-BZCYYb membrane was tested in concentrated H₂O and CO₂ for hundreds of hours, there was dramatic microstructure reconstruction and formation of a porous layer as deep as ~0.33 mm [14]. If the thickness was in the order of tens of microns, the membrane should have already failed mechanically, which means that asymmetric Ni-BZCYYb membranes could not survive in wet CO₂ for a long time. The microstructure reconstruction is due to the cooperative effect of decomposition of BZCYYb in wet CO₂ and Ni dusting in concentrated CO. After RWGS reaction, there were 11.5% H₂O and 8.5% CO in wet 40% H₂ and 30% CO₂ at 900 °C. High concentration of water vapour promoted the reaction between BZCYYb and CO₂, creating porosity in the membrane. High concentration of CO can easily

penetrate through the porosity created by the decomposition of BZCYYb phase, and cause the carbon-induced metal dusting. Therefore, the size of Ni particles was greatly increased and the membrane structure was reconstructed, impairing the long-term mechanical stability of the membrane. In Ni-BZY4 membrane, there are no such issues because of the excellent stability of BZY in CO₂ and low CO content. Because the BZY phase is very stable and compact, low content of CO cannot penetrate into the inside of Ni-BZY4 membrane and the Ni particles don't grow larger, as observed in Fig. 7. Therefore, the Ni-BZY4 membrane is expected to have a much better long-term performance and mechanical stability than that of Ni-BZCYYb membrane. The flux can be further improved by reducing the thickness of the membrane, e.g., fabrication of asymmetric membrane. More importantly, the exceptional chemical and mechanical stability makes the asymmetric membrane really viable even in harsh operating conditions.

3.5 Implication on the feasibility of using BZYNiO₂ as electrolyte for SOFCs

An important implication of this study is that BaY₂NiO₅ can react with CO₂ forming BaCO₃ and Y₂O₃, this may be a serious problem for BZYNiO₂, which is proposed as a promising electrolyte material with great sinter-activity and high electrical conductivity [37,38,49]. Until now, no study has been reported on its chemical stability, which is crucial for its successful application. Rietveld refinements of the XRD profiles in Fig. 8a shows that fresh BZYNiO₂ consists of BZY and BaY₂NiO₅, consistent with the reports of Tong *et al.* [37]. After annealing in wet CO₂ at 700 °C for 100 h, BaY₂NiO₅ disappears but BaCO₃ and Y₂O₃ are found (Fig. 8b). SEM image in Fig. 9a shows that the polished surface of BZYNiO₂ before exposure to CO₂ is very dense. It is noticeable that some dark spots are randomly distributed in the ceramic matrix. EDX spectra in Fig. 10a and b show that the dark phase consists of Ba, Y, Ni, and O, while the

light phase consists of Ba, Zr, Y, and O. Considering the XRD results, the dark and light phases are BaY_2NiO_5 and BZY, respectively. After annealing in wet CO_2 , the surface of BZYNiO2 is covered by many crystal-like particles with a size ranging from hundreds of nanometers to a few microns, as shown in Fig. 9b. The EDX spectrum in Fig. 10c shows that the particles mainly contain Ba, C, Y, and O, suggesting that they are BaCO_3 and Y_2O_3 . It can be seen from the coverage that the amount of BaCO_3 and Y_2O_3 is much more than that of BaY_2NiO_5 on the fresh membrane surface, probably due to diffusion of Ba^{2+} from BaY_2NiO_5 inside the BZYNiO2 ceramic. One may ask whether Ba-excessive BZY contribute to the formation of BaCO_3 . This is unlikely because there should be a significant change in the lattice parameter if Ba-excessive BZY reacts with CO_2 , however, there is almost no change in the lattice parameter of BZY phase (obtained from Rietveld refinement of XRD profiles of BZYNiO2 before and after the annealing in wet CO_2 , 4.208 and 4.206 Å, respectively, Fig. 8a and b). These results clearly suggest that BaY_2NiO_5 in BZYNiO2 makes it chemically unstable in $\text{H}_2\text{O}/\text{CO}_2$, which needs to be resolved before it is used as electrolyte for solid oxide fuel cells. This problem may be solved by a similar strategy as that in Ni-BZY4. BZYNiO2 prepared by solid state reaction method can cause the formation of BaY_2NiO_5 which is an efficient sintering aid but also cause chemical instability, and BZY prepared by CEC method is chemically stable but not sinter-active. The combination of these powders can lead to a chemically stable yet still sinter-active proton conductor.

4. Conclusions

Although BZY possesses excellent chemical stability in H_2O and CO_2 , BZY ceramic and Ni-BZY membranes sintered using NiO sintering aid are chemically unstable because of the formation of BaY_2NiO_5 . BaY_2NiO_5 reacts with H_2 , H_2O , and CO_2 , forming insulating BaY_2O_4 , $\text{Ba}(\text{OH})_2$, and BaCO_3 phases, respectively. Previous report suggested that BaY_2NiO_5 was

reduced to BaO and Y₂O₃, which were dissolved back to BZY lattice. However, we find that Ni-BZY membranes contain BaY₂O₄ islands after reduction. Both BaY₂NiO₅ and BaY₂O₄ easily react with H₂O and CO₂ forming Ba(OH)₂ and BaCO₃, respectively. Therefore, both BZYNiO₂ and Ni-BZY are chemically unstable in wet CO₂, and the hydrogen flux of Ni-BZY membranes degraded significantly in wet H₂ at 900 °C. A comparative study shows that the more BaY₂O₄ there is in Ni-BZY membranes, the less stable they are. The chemical instability greatly restricts the applications of BZYNiO₂ and Ni-BZYNiO₂ as electrolytes for solid oxide fuel cells and hydrogen separation membranes, respectively. Fortunately, the chemical stability of Ni-BZY membranes can be improved by reducing the amount of BaY₂O₄ formed in the fabrication process. This is achieved by replacing a portion of BZY20 powder in the starting material with BZY20-CEC powder. The BZY20-CEC grains also act as a covering layer for BaY₂O₄ and helps avoid the reaction between BaY₂O₄ and H₂O/CO₂. The new Ni-BZY4 membrane fabricated with 20% BZY20-SSR and 80% BZY20-CEC powders demonstrated very stable and improved permeation flux in wet 50% CO₂ at 900 °C. The phase composition and membrane microstructure were also intact after the test, indicating its excellent chemical stability, surpassing previous Ni-BZCYYb membrane. It also possesses much higher hydrogen flux than Ni-BZPY. These facts demonstrate that Ni-BZY4 is very promising for hydrogen permeation applications.

Supplementary data

Cross-sectional SEM images of Ni-BZY membranes, XRD patterns of fresh and tested Ni-BZY1 membrane, SEM images of tested Ni-BZY1 membrane, SEM-EDX analysis of polished/polished and etched surfaces of Ni-BZY1 membrane, SEM-EDX analysis of surface of

Ni-BZY1 membrane after boiling or annealing in wet CO₂, Rietveld refinement profile of BaY₂NiO₅ powder, XRD pattern from feed surface of Ni-BZY4 membrane after permeation test in wet 50% CO₂.

This material is available free of charge via the Internet at <http://www.sciencedirect.com>.

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Tabel 1. List of abbreviations for Ni-BZY (volume ratio 40:60) membranes prepared with different types and amounts of BZY powders.

Abbreviation	BZY powders
Ni-BZY1	BZYNiO ₂
Ni-BZY2	BZY20-SSR
Ni-BZY3	40% BZY20-SSR, 60% BZY20-CEC
Ni-BZY4	20% BZY20-SSR, 80% BZY20-CEC

Table 2. Lattice constants of phases in fresh and annealed BZYNiO₂ determined by Rietveld refinement of XRD patterns in Fig. 8.

Sample	Phase	Unit cells	Lattice constants (Å)
Fresh BZYNiO ₂	BZY	Cubic ($Pm\bar{3}m$)	4.208
	BaY ₂ NiO ₅	Orthorhombic (Immm)	a=3.757, b=5.755, c=11.320.
Annealed BZYNiO ₂	BZY	Cubic ($Pm\bar{3}m$)	4.206
	BaCO ₃	Orthorhombic (Pmcn)	a=5.306, b=8.891, c=6.471.
	Y ₂ O ₃	Cubic ($Ia\bar{3}$)	10.595

Figure captions

Fig. 1. Schematic for the synthesis and chemical stability test processes of (a) BZYNiO₂ and Ni-BZYNiO₂ (denoted as Ni-BZY1 in Table 1), (b) BaY₂NiO₅.

Fig. 2. Time dependence of hydrogen flux of Ni-BZY membranes prepared by different methods measured in wet 20% H₂ at 900 °C. All membrane thickness is 0.40 mm.

Fig. 3. SEM images obtained from polished surfaces of Ni-BZY1 (a, e, i), Ni-BZY2 (b, f, j), Ni-BZY3 (c, g, k), and Ni-BZY4 (d, h, l) membranes. (a-d): polished, (e-h): polished and boiled for 20 h, (i-l): polished and annealed in wet 17% H₂ and 80% CO₂ at 900 °C for 50 h.

Fig. 4. XRD patterns obtained from surfaces of Ni-BZY1 after boiling for 20 h (a), Ni-BZY1 (b), Ni-BZY2 (c), Ni-BZY3 (d), and Ni-BZY4 (e) membranes after annealing in wet 17% H₂ and 80% CO₂ at 900 °C for 50 h. b: BZY (JCPDS 06-0399), n: Ni (JCPDS 04-0850), c: BaCO₃ (JCPDS 05-0378), y: Y₂O₃ (JCPDS 41-1105).

Fig. 5. XRD patterns of fresh BaY₂NiO₅ powder (a), BaY₂NiO₅ powder after annealing in CO₂ at 900 °C for 10 h (b), BaY₂NiO₅ powder after annealing in dry H₂ at 900 °C for 20 h (c), BaY₂NiO₅ powder after annealing in wet H₂ at 900 °C for 20 h (d). b: BaY₂NiO₅ (JCPDS 41-0463), c: BaCO₃, y: Y₂O₃, n: NiO (JCPDS 78-0643), B: BaY₂O₄ (JCPDS 82-2319), N: Ni.

Fig. 6. Time dependence of hydrogen flux of a 0.40-mm-thick Ni-BZY4 membrane in wet 40% H₂ with different contents of CO₂ at 900 °C.

Fig. 7. SEM images of Ni-BZY4 after permeation test in wet 50% CO₂ at 900 °C. (a) Cross-sectional view of whole membrane, (b) top view of feed side surface, (c) cross-sectional view

close to feed side surface, (d) cross-sectional view close to sweep side surface. Membrane was polished prior to SEM study.

Fig. 8. Rietveld refinement for XRD patterns obtained from surfaces of sintered BZYNiO₂ pellets before (a) and after (b) treatment in wet CO₂ at 700 °C for 100 h. The unit cells and lattice constants are summarized in Table 2.

Fig. 9. SEM images of polished surface of BZYNiO₂ pellets before (a) and after treatment (b) in wet CO₂ at 700 °C for 100 h.

Fig. 10. EDX spectra obtained from spots 1 (a), 2 (b), and 3 (c) in Fig. 9.

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Fig. 6. Time dependence of hydrogen flux of a 0.40-mm-thick Ni-BZY4 membrane in wet 40% H₂ with different contents of CO₂ at 900 °C.

Fig. 7. SEM images of Ni-BZY4 after permeation test in wet 50% CO₂ at 900 °C. (a) Cross-sectional view of whole membrane, (b) top view of feed side surface, (c) cross-sectional view close to feed side surface, (d) cross-sectional view close to sweep side surface. Membrane was polished prior to SEM study.

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