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Effect of Zr-Doping on the Chemical Stability and Hydrogen Permeation of the Ni−$BaCe_{0.8}Y_{0.2}O_{3-\alpha}$ Mixed Protonic−Electronic Conductor

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Successful development of hydrogen separation membranes based on mixed ionic and electronic conductors may improve the economics of hydrogen production. While high proton conductivity has been reported for many perovskite-type oxides in a humid atmosphere, materials with both high proton conductivity and good chemical stability under conditions for practical hydrogen separation are yet to be developed. In this paper, we report the effect of Zr-doping in BZCYs [$Ba(Zr_{0.8-x}Ce_xY_{0.2})O_{3-\alpha}$] ($0.4 \le x \le 0.8$) on the proton conductivity and chemical stability. A novel Ni−BZCY7 [Ni−$Ba(Zr_{0.1}Ce_{0.7}Y_{0.2})O_{3-\alpha}$] cermet (metal−ceramic composite) membrane appears to have not only high proton conductivity but also adequate stability in a CO_2- and H_2O-containing atmosphere.

Introduction

A worldwide energy crisis and the ever-increasing environmental concerns are strong incentives for using hydrogen as a sustainable and clean energy source.[1] Although hydrogen must be ultimately produced from renewable sources, fossil fuels are still the economically feasible sources of hydrogen in the interim. Development of a membrane-based separation and purification process is of particular interest for applications in advanced fossil-based power and fuel technologies.

Compared with traditional gas separation technologies, hydrogen separation based on a dense, mixed-conducting membrane is projected to be more cost-effective.[2,3] These membranes separate hydrogen from mixed gases at commercially significant rates under industrially relevant conditions (operating temperatures up to 900°C), without the need for electrodes or electrical circuitry.

High proton conductivity has been reported for many perovskite-type oxides in a humid atmosphere, including $BaZrO_3$, $SrZrO_3$, $SrCeO_3$, and $BaCeO_3$ doped with a rare-earth oxide.[4,5] However, materials with both high proton conductivity and adequate chemical stability are yet to be developed.[6] Yttrium-doped barium cerate (BCY) is one of the best proton conductors among this class of conductors.[7] However, exposure to CO_2- and H_2O-containing atmospheres, which would be present under conditions similar to those of practical applications, will degrade the performance of the material because of the formation of insulating barium carbonate ($BaCO_3$) and cerium oxide (CeO_2).[8−10] In contrast, yttrium-doped barium zirconates have good chemical stability but are undesirable because of their relatively low conductivity and high sintering temperature.[11,12] Since $BaCeO_3$ and $BaZrO_3$ easily form solid solutions, it is possible to replace any desired fraction of the Ce in $BaCeO_3$ with Zr; the solid solution between cerate and zirconate of proper composition may have both high protonic conductivity and adequate chemical stability.[13,14] In this paper, we report the effect of Zr-doping on the hydrogen permeation and chemical stability of barium cerate−Ni cermet membranes under various conditions.

Experimental Section

The BZCYs [$Ba(Zr_{0.8-x}Ce_xY_{0.2})O_{3-\alpha}$] ($0.4 \le x \le 0.8$) were prepared by a solid-state reaction method. Stoichiometric amounts of high-purity barium carbonate, cerium oxide, zirconium oxide, and yttrium oxide powders were mixed for 48 h by ball-milling with stabilized zirconia media in isopropyl alcohol (IPA). The resultant mixture was then dried and calcined at 1050 °C in air for 10 h to form the perovskite phase. The calcinations and ball-milling procedures were repeated until a single phase was obtained, as confirmed by X-ray diffraction. The BZCY powders were then

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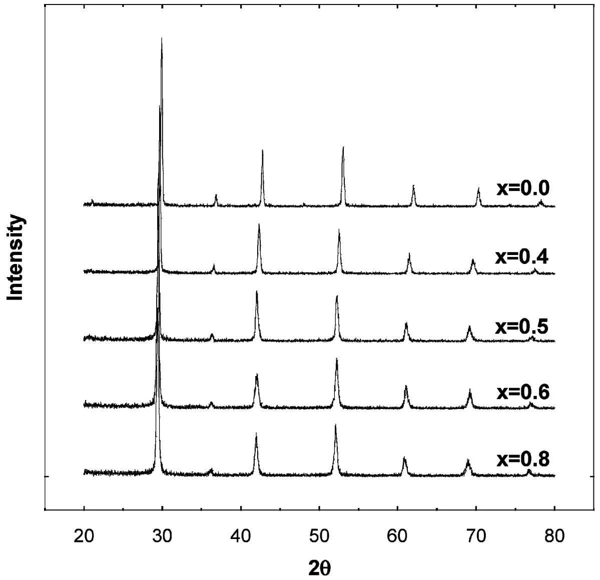

Figure 1. X-ray diffraction patterns of $Ba(Zr_{0.8-x}Ce_xY_{0.2})O_3$ ($0.0 \leq x \leq 0.8$).

ground and mixed with nickel powder at a volume ratio of ceramic to nickel of 1.5. The mixed powders were then pressed at 250 MPa into pellets with a diameter of 2.2 cm. The green pellets were sintered at 1400−1420 °C for 10 h in dry 4% hydrogen balanced with nitrogen.

For permeation and stability tests, both sides of the sintered disks with a diameter of 1.8 cm were ground using 600-grit SiC paper to obtain the desired thickness and produce faces that were flat and parallel to one another. Gold rings were used as the seal, and the active areas of the samples for hydrogen permeation were around 1.13 cm^2. The hydrogen permeation rates (i.e., hydrogen flux) were measured using a procedure as described elsewhere.[15] Hydrogen leakage through the seal was corrected by measuring the helium concentration in the permeate stream. The stability of membranes in wet CO_2-containing atmospheres was determined by measuring the hydrogen flux versus time in atmospheres with different concentrations of CO_2. The typical hydrogen leakage rates were <10% of the total permeation rates. The composition and microstructure of membranes were examined using a scanning electron microscope (JEOL JSM-5400) equipped with an energy dispersion X-ray (EDX) analyzer.

Results and Discussion

Shown in Figure 1 are X-ray diffraction patterns of sintered $Ba(Zr_{0.8-x}Ce_xY_{0.2})O_3$ with $0 \leq x \leq 0.8$, suggesting that solid solutions with $x = 0-0.8$ were formed. However, there was no indication of Zr^{4+} and Ce^{4+} ordering on the B-site of the structure, in agreement with the work of others.[13,14] It can be seen that, as the Zr content increased, the peak position shifted to higher angles, indicating that the perovskite unit cell volume decreased as the smaller Zr^{4+} ion ($R^{IV} = 0.72$ Å) replaced the larger Ce^{4+} ($R^{IV} = 0.87$ Å)[16] ion. The absence of low-angle supercell reflections indicates a random B-site cation distribution.

Like BCY, the hydrogen flux through BZCY alone is expected to be very small, because its electronic conductivity is relatively low.[17,18] To increase the electronic conductivity and thereby enhance the hydrogen flux, we have developed cermet Ni−BZCY (i.e., metal−ceramic composite) membranes, in which 40 vol % nickel is dispersed in a ceramic matrix. The hydrogen flux through the cermet membranes is most likely limited by proton transport through the BZCY phase because the effective protonic conductivity of the membrane is much smaller than the effective electronic conductivity.

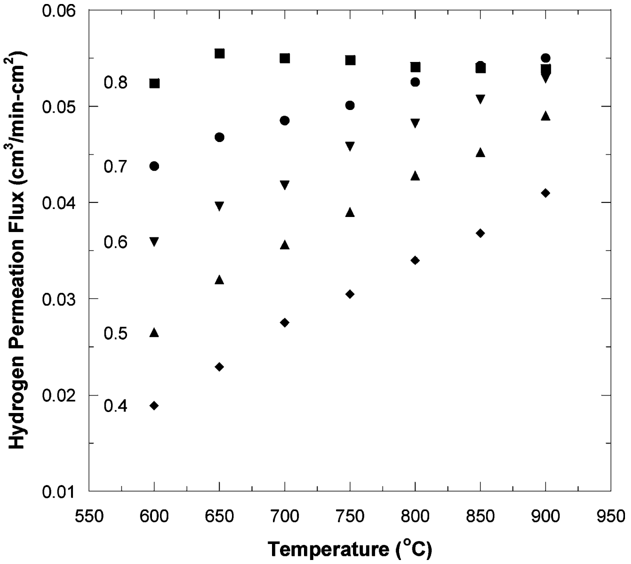

Figure 2. Hydrogen permeation fluxes through 1.0 mm thick Ni−Ba($Zr_{0.8-x}Ce_xY_{0.2}$)O_3($0.4 \leq x \leq 0.8$) membranes using wet 4% H_2 (balance He) as the feed gas and 100 ppm H_2 (balance N_2) as the sweep gas. The number adjacent to each set of data points represents the value of *x* in the formula for BZCY.

Figure 2 shows the hydrogen flux as a function of temperature for Ni−$Ba(Zr_{0.8-x}Ce_xY_{0.2})O_{3-\alpha}$ cermet membranes (∼1 mm thick) with $0.4 \leq x \leq 0.8$. The feed gas was wet 4% hydrogen in helium, and the sweep gas contained 100 ppm hydrogen balanced with nitrogen. The hydrogen permeation fluxes for Ni−BZCY membranes of all compositions increased with temperature from 600 to 900 °C, but those for the Ni−BCY membranes reached a maximum of 0.056 cm^3/(min cm^2) at 650 °C and then decreased slightly with temperature. The permeation flux decreased with the content of zirconium from 10% to 40% at each fixed temperature, but it was comparable to that of Ni−BCY for the Ni−BZCY membranes with a small amount of zirconium ($x = 0.6$ and 0.7). For the Ni−BZCY7 ($x = 0.7$) sample, the fluxes were only slightly lower than those of Ni−BCY at low temperatures and slightly higher at high temperature (900 °C). For the Ni−BZCY6 ($x = 0.6$) sample, the fluxes were nearly the same as those for Ni−BCY at high temperatures. The highest flux (0.056 cm^3/(min cm^2)) was measured for the Ni−BZCY7 sample at 900 °C.

Figure 3 shows the effect of water vapor on the hydrogen permeation flux of Ni−BCY, Ni−BZCY7, and Ni−BZCY6 cermet membranes with a thickness of ∼0.5 mm. The feed gas was composed of 4% hydrogen balanced with helium,

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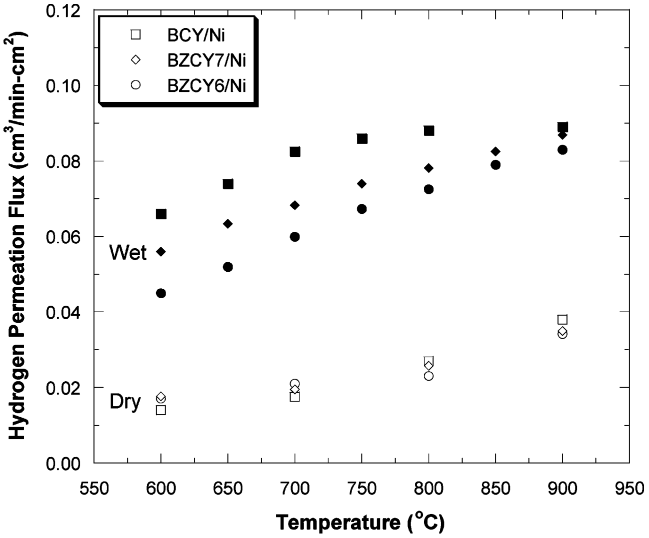

Figure 3. Hydrogen flux through 0.5 mm thick Ni−Ba($Zr_{0.8-x}$ $Ce_xY_{0.2}$)O_3 ($0.6 \leq x \leq 0.8$) membranes using dry and wet 4% H_2 (balance He) as the feed gas.

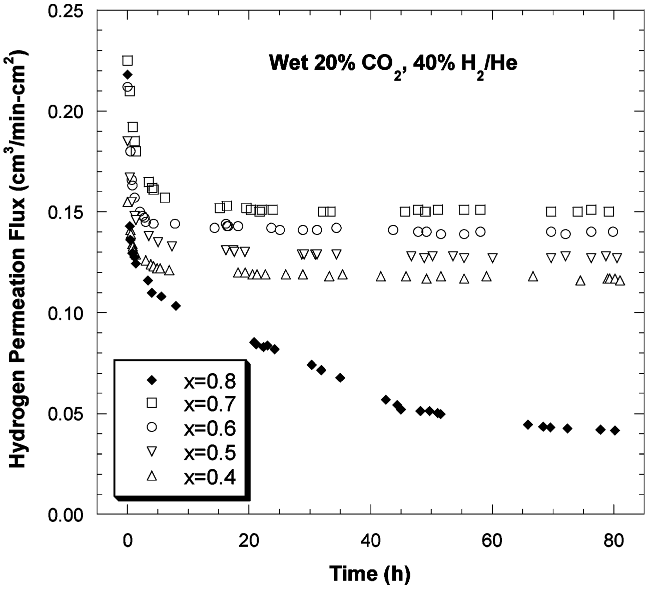

Figure 4. Time dependence of hydrogen flux through 0.75 mm thick Ni−BZCY ($0.4 \leq x \leq 0.8$) membranes in a feed gas of wet 20% CO_2 (balance 40% H_2/He) at 900 °C.

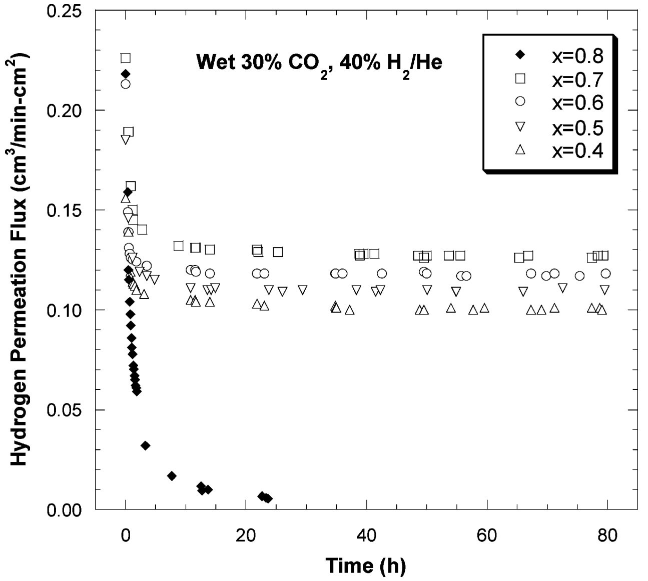

Figure 5. Time dependence of hydrogen flux through 0.75 mm thick Ni−BZCY ($0.4 \leq x \leq 0.8$) membranes in a feed gas of wet 30% CO_2 (balance 40% H_2/He) at 900 °C.

and the sweep gas contained 100 ppm hydrogen balanced with nitrogen. The hydrogen flux was measured in the temperature range of 600−900 °C under both dry and wet conditions (for wet conditions, an about 3% water vapor concentration was obtained by bubbling the gas through deionized water at room temperature). The hydrogen permeation fluxes increased with temperature under both dry and wet conditions for all samples. Also, the hydrogen permeation fluxes were much higher under wet than dry conditions. The permeation fluxes for Ni−BZCY7 and Ni−BZCY6 were almost the same as those for Ni−BCY under dry conditions in the entire temperature range studied, but reached 0.087 and 0.082 cm^3/(min cm^2) at 900 °C when a wet feed gas was used, which is only slightly lower than that for Ni−BCY at 900 °C. Moisture in the feed gas will not increase the conductivity of Ni (in fact, it may decrease the conductivity of Ni by oxidizing the surface), but will reduce the partial pressure of hydrogen in the feed gas. However, the presence of water vapor in the feed gas may enhance the proton conductivity as well as the surface catalytic activity of the ceramic phase of the membrane, leading to increased hydrogen permeation fluxes. To study the effect of Zr-doping on the chemical stability of BZCY in H_2O- and CO_2-containing atmospheres, we monitored the hydrogen fluxes through Ni−BZCY membranes as a function of time after the feed gas was switched from H_2 to wet CO_2-containing gas. All samples were ∼0.75 mm thick and were tested using wet feed gas that contained 20% and 30% CO_2 at 900 °C. Each feed gas also contained 40% H_2 with a balance of He, which was prepared using mass flow controllers to blend UHP H_2 and He with CO_2. The sweep gas contained 100 ppm hydrogen balanced with nitrogen. For measurements with a given CO_2 concentration, the initial reading (time 0 h) was taken with wet 40% H_2 (balance He) as the feed gas.

Figure 4 shows the hydrogen flux versus time through the Ni−Ba($Zr_{0.8-x}Ce_xY_{0.2}$)$O_{3-\alpha}$ membranes with x in the range 0.4−0.8. For the Ni−BCY sample without Zr-doping ($x = 0.8$), the flux decreased quickly after the feed gas was switched to 20% CO_2 gas at 900 °C; it decreased ∼48% after 6 h of exposure and continued to decrease with time of exposure. In contrast, the membranes with Zr-doping ($0.4 \leq x \leq 0.7$) behaved very differently when exposed to a wet gas containing 20% CO_2. The hydrogen flux decreased moderately in the first several hours of exposure. The initial (time 0 h) flux drops increased from ∼24% to ∼33% with zirconium content decreasing from 40% to 10%, but after this initial decrease, the hydrogen fluxes were stable for 80 h. The Ni−BZCY7 membrane displayed the highest flux (0.15 cm^3/(min cm^2)) in an atmosphere containing 20% CO_2.

To determine the stability of the Ni−BZCY7 membranes in an atmosphere containing an even higher concentration of CO_2, we also measured hydrogen permeation fluxes through Ni−Ba($Zr_{0.8-x}Ce_xY_{0.2}$)$O_{3-\alpha}$ membranes ($0.4 \leq x \leq 0.8$) when they were exposed to a wet feed gas containing

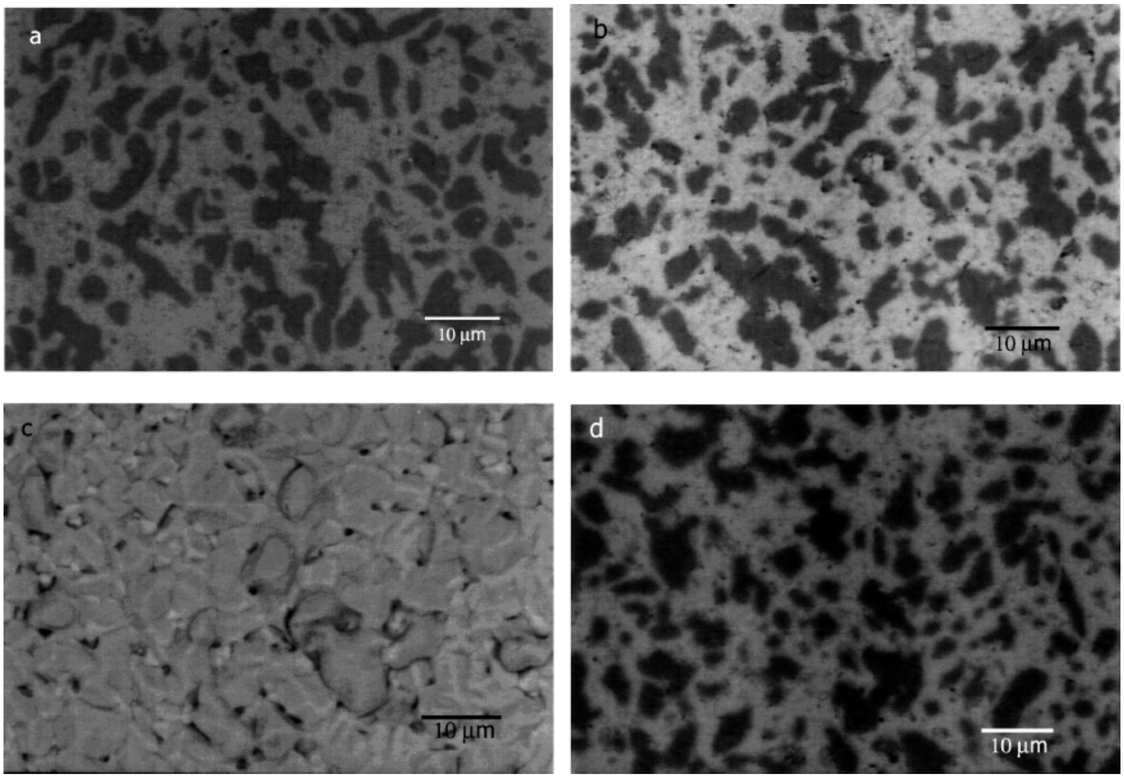

Figure 6. Backscattered electron images of the surfaces of the Ni−BCY and Ni−BZCY membranes: (a) Ni−BCY and (b) Ni−BZCY before exposure to the feed gas, (c) Ni−BCY and (d) Ni−BZCY after exposure to a wet feed gas containing 30% CO_2 at 900 °C for 25 h (dark- and light-colored phases are metal and ceramic, respectively).

30% CO_2 at 900 °C. As shown in Figure 5, the hydrogen fluxes for these membranes were stable for 80 h after an initial decrease. It is noted that the initial drops in hydrogen fluxes increased from ∼35% to ∼45% as the zirconium content was decreased from 40% to 10%, similar to the behavior observed in the wet gas containing 20% CO_2. For the membranes without Zr-doping ($x = 0.8$), the hydrogen flux decreased even more sharply upon exposure to a gas containing 30% CO_2; it decreased ∼53% within the first hour of exposure, ∼72% after 2 h of exposure, and ∼91% after 7 h of exposure and continued to degrade with time until there was no observable hydrogen permeation flux. After 25 h of exposure to a wet feed gas containing 30% CO_2 at 900 °C, we found the surface of the sample in the feed gas side became insulating. Figure 6 shows some typical SEM images of the surfaces of Ni−BCY and Ni−BZCY7 membranes before and after exposure to a wet feed gas containing 30% CO_2. Before the stability test, the surface of Ni−BCY (Figure 6a) or Ni−BZCY7 (Figure 6b) has two distinct regions; the dark region is Ni metal, whereas the white region is the BCY or BZCY7 ceramic phase. After the stability test, the surface of the Ni−BCY membrane was completely covered by a layer of barium carbonate (white, electronically insulating), as shown in Figure 6c. The formation of barium carbonate due to the reaction between BCY and CO_2 led to a sharp drop in the hydrogen flux. In contrast, the surface of Ni−BZCY7 showed little change after the stability test, as seen in Figure 6d. Clearly the stability of the membranes was improved by the doping of Zr.

Conclusions

B-site substitution of Ce by Zr in BCY dramatically enhanced the chemical stability of the Ni−BZCY membranes in a CO_2- and H_2O-containing atmosphere, although it slightly reduced the hydrogen permeation rate at high temperatures (e.g., 900 °C). While the hydrogen permeation fluxes through a Ni−BCY membrane degraded rapidly and continuously upon exposure to a wet CO_2-containing atmosphere, those through a Ni−BZCY membrane remained relatively stable for 80 h in an atmosphere containing up to 30% CO_2 at 900 °C after a small initial decrease. Although the hydrogen permeation fluxes of Ni−BZCY cermet membranes decreased with zirconium content at a given temperature, they are comparable to those of Ni−BCY membranes when the zirconium content is sufficiently low (e.g., $x = 0.6, 0.7$). Among all compositions studied, Ni−$Ba(Zr_{0.8-x}Ce_xY_{0.2})O_{3-\alpha}$ with $0.4 \leq x \leq 0.7$, the Ni−BZCY7 ($x = 0.7$) composition exhibited both a high H_2 permeation rate and adequate stability, thus having potential for practical applications.

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