Composite Ni–Ba(Zr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$)O$_3$ membrane for hydrogen separation

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Abstract

Composite membranes consisting of Ni metal and Ba(Zr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$)O$_3$ (or Ni–BZCY7) have been developed for separation of hydrogen from gas mixtures to replace Ni–BCY20 (Ni–BaCe$_{0.8}$Y$_{0.2}$O$_3$), which has poor stability in CO$_2$ and H$_2$O-containing atmosphere. Hydrogen fluxes through these cermet membranes were measured as a function of temperature, membrane thickness, and partial pressure of hydrogen in various atmospheres. Results indicated that the Ni–BZCY7 membrane is chemically stable and display high hydrogen permeability. A maximum flux of 0.805 cm^3 min^{-1} cm^2 was obtained for a dense cermet membrane of 266-μm-thick at 900 °C using 100% H$_2$ as the feed gas and 100 ppm H$_2$/N$_2$ as the sweep gas. The stable performance of Ni–BZCY7 cermet membrane during exposure to a wet gas containing 30% CO$_2$ for about 80 h indicated that it is promising for practical applications.
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1. Introduction

While hydrogen is mainly used as a chemical feedback today, it is expected to become the fuel for both electric power generation and transportation in the future because of the energy crisis and the increasingly intense environmental concerns. Producing hydrogen from fossil and renewable resources would diversify the domestic energy supply and help to reduce dependence on foreign sources. Under the support of Hydrogen Fuel Initiative, hydrogen production and distribution technologies are being developed for powering vehicles and stationary power generation plants. High performance hydrogen separation membranes are likely to play an essential role in fulfilling this mission.

The goal is to develop a dense, ceramic-based mixed ionic and electronic conductor (MIEC) membrane that is highly selective, chemically stable in practical environments at temperatures up to ≈900 °C, and can separate hydrogen from mixed gases (particularly product streams generated during coal gasification, methane partial oxidation, reforming, and water-gas shift reactions) at commercially significant fluxes, without the need for electrodes or electrical circuitry.

High proton conductivity has been reported for many perovskite-type oxides such as doped-BaZrO$_3$, SrZrO$_3$, SrCeO$_3$, and BaCeO$_3$ in humid atmospheres [1,2]. Our early effort focused on BCY20 (BaCe$_{0.8}$Y$_{0.2}$O$_3$) because of its high proton conductivity [3]. However, exposure to CO$_2$ and H$_2$O-containing atmospheres, as would be present in a practical environment, will degrade the material as it reacts to form insulating barium carbonate (BaCO$_3$) and cerium oxide (CeO$_2$) [4–6]. In contrast, yttrium-doped barium zirconates have good chemical stability but are undesirable because of their relatively low conductivity and high sintering temperature [7,8]. Achieving both high proton conductivity and good chemical stability, which is a prerequisite for practical applications, is generally considered to be a grand challenge [9]. Since both BaCeO$_3$ and BaZrO$_3$ easily form solid solutions, it may be possible to replace any desired fraction of the Ce in BaCeO$_3$ with Zr, and thereby achieve a solid solution between cerate and zirconate with both high protonic conductivity and good chemical stability [10,11].

In this paper, we report BZCY7 [Ba(Zr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$)O$_3$] as a possible alternative to BCY20. The hydrogen transport properties and chemical stability of Ni–BZCY7 cermet membranes were studied under various conditions.

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2. Experimental

The BCY20 (BaCe$_{0.8}$Y$_{0.2}$O$_3$) and BZCY7 [Ba(Zr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$)O$_3$] 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 by ball-milling with stabilized zirconia media in isopropyl alcohol for 48 h. The resultant mixture was then dried and calcined at 1050 °C in air for 10 h to form the perovskite phase. The calcined oxides were ball-milled for 24 h and calcined again at 1050 °C in air for 10 h. After confirming a single phase by X-ray diffraction, the ceramic powders were ground and mixed with nickel powder at a volume ratio of ceramic to nickel equal to 1.5. The mixed powders were then pressed uniaxially 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 4% hydrogen balanced with nitrogen.

For permeation and stability tests, both sides of the disks were polished using 600-grit SiC paper to obtain the desired thickness and produce faces that were flat and parallel to one another. The hydrogen permeation rate (i.e., hydrogen flux) was measured using a procedure described elsewhere [12]. The hydrogen leakage rate following this procedure was typically <10% of the total permeation flux. 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$_2$.

3. Results and discussion

3.1. Hydrogen transport properties of Ni–BZCY7 cermet membrane

The hydrogen flux through BZCY7 is expected to be very small, because its electronic conductivity is relatively low, preventing a high nongalvanic hydrogen flux. To increase the electronic conductivity and thereby enhance the hydrogen flux, we have developed a cermet (i.e., ceramic–metal composite) membrane, in which 40 vol.% of nickel is dispersed in a ceramic matrix. From the back-scattered electron image of a Ni–BZCY7 surface (Fig. 1), we can clearly see that the membrane is dense and that the metal phase is randomly distributed in the oxide matrix (the dark region is Ni, the white region is BZCY7). In this cermet membrane, the nickel phase enhances the hydrogen permeability of the ceramic phase by increasing the electronic conductivity of the composite, surface exchange kinetics, and improving mechanical stability. The cermet membrane was conductive at room temperature, suggesting the formation of a three-dimensional network of the Ni phase. Thus, the hydrogen flux through the membranes should be limited by proton transport through BZCY7 phase.

From the hydrogen concentration measured in the sweep side of the permeation assembly and the sweep gas flow rate, the total hydrogen permeation rate was calculated from equation assuming the idea gas law. The hydrogen permeation flux was calculated by dividing the permeation rates by the surface area of the disk membranes. Hydrogen leakage through any incomplete
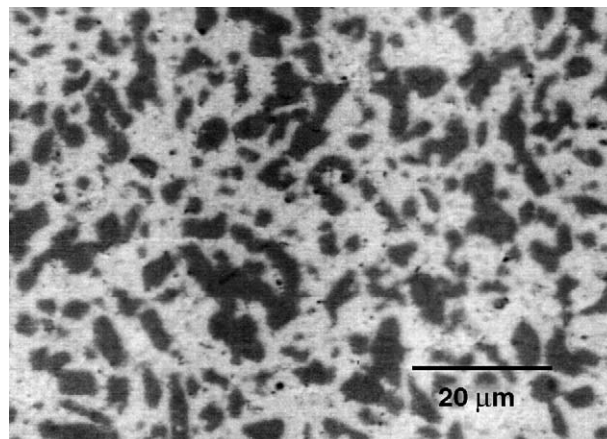

Fig. 1. Back-scattered electron image of the Ni–BZCY7 cermet membrane surface.

seal was corrected by measuring the helium concentration of the permeate stream.

Fig. 2 shows the temperature dependence of hydrogen flux through a cermet membrane with thickness of ∼1 mm. The feed gas was composed of 4% H$_2$/He, and the sweep gas contained 100 ppm hydrogen balanced with nitrogen. For the Ni–BZCY7 sample, the hydrogen flux increased as the temperature was increased from 600 to 900 °C under both dry and wet conditions, and reached 0.056 cm^3 min^{-1} cm^2 at 900 °C using wet 4% H$_2$/balance He as the feed gas. In comparison with the Ni–BCY20 sample, the flux through the Ni–BZCY7 sample was almost the same under the dry condition, and only slightly lower at low temperature and even a little higher at 900 °C under the wet condition. Fig. 2 also shows that the fluxes under the wet condition were much higher than under the dry condition at same temperature for both samples, and that the addition of moisture to the atmosphere increased the permeation rate by a factor of 4 at 600 °C and by a factor of 3 at 900 °C for the Ni–BZCY7 sample. Moisture is not expected to increase the hydrogen flux
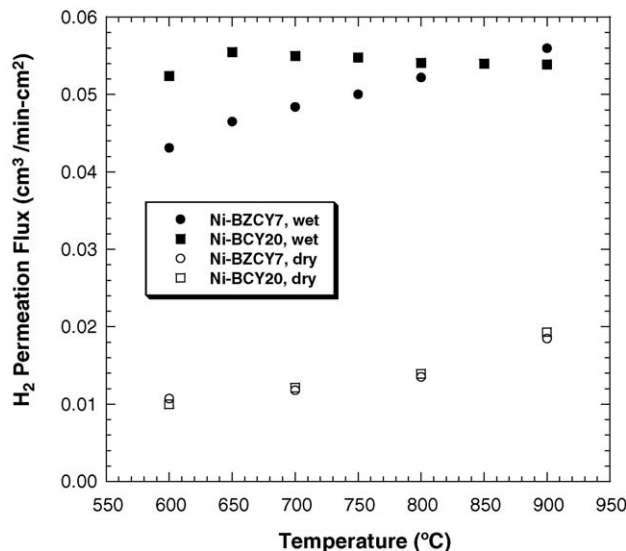

Fig. 2. Hydrogen flux through a 978-μm-thick Ni–BZCY7 membrane using dry and wet 4% H$_2$ (balance He) as feed gas.

through the metal and may actually decrease it by oxidizing the metal surface, thereby reducing the partial pressure of hydrogen in the feed gas. On the other hand, moisture is expected to increase the permeation rate of the ceramic phase by increasing its proton conductivity and enhancing interfacial reaction kinetics. This fact proved that the proton mainly transports through the ceramic phase of the membrane instead of metal phase under wet condition.

Shown in Fig. 3 is the effect of hydrogen partial pressure on hydrogen permeability at 900 °C. The hydrogen flux of a 266-μm-thick membrane is plotted as a function of $\Delta pH_2^{0.5}$, the difference in the square root of the hydrogen partial pressure in the feed and sweep gases. For a feed gas of ~100% H_2, the leakage was calculated from the measured leakage using a feed gas of 80% H_2. Since the membrane thickness is fairly thin, the flux through the Ni metal phase can no longer be ignored, especially when $\Delta pH_2^{0.5}$ is high. The hydrogen flux going through the ceramic phase (after being corrected by the flux through Ni phase) is also showed in Fig. 3. The flux through the Ni metal phase becomes more important when $\Delta pH_2^{0.5}$ is high, but quite small compared with the flux transported through the ceramic phase. Both of the hydrogen fluxes increased with $\Delta pH_2^{0.5}$, because the driving force for proton permeation increases with $\Delta pH_2^{0.5}$.

Shown in Fig. 4 is the temperature dependence of the hydrogen flux of the 266-μm-thick cermet membrane with a feed gas of ~100% H_2. As the temperature was increased from 600 to 900 °C, the hydrogen permeation flux increased from 0.505 to 0.805 $cm^3\,min^{-1}\,cm^2$. Since the electronic conductivity of the nickel phase decreases with increasing temperature, these results further confirm that the hydrogen flux through the Ni–BZCY7 cermet membrane is limited by the proton transport through the ceramic BZCY7 phase, which is also consistent with Fig. 2.
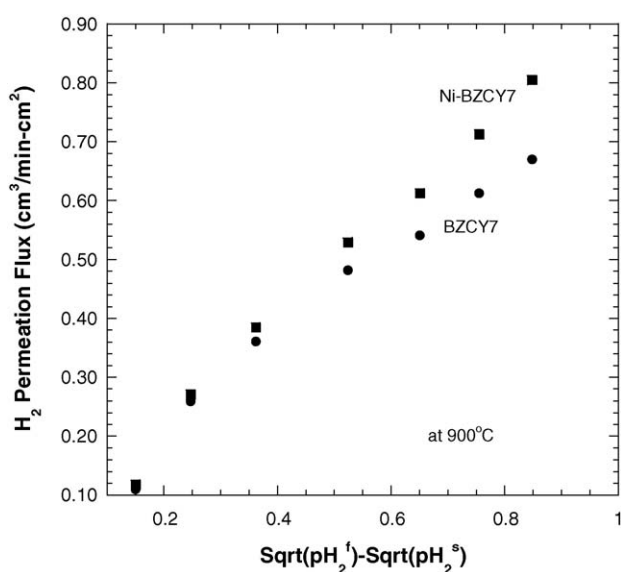

Fig. 4. Temperature dependence of hydrogen flux of 266-μm-thick Ni–BZCY7 membrane when feed gas was ~100% H_2.

The temperature dependence of hydrogen flux for membranes of different thicknesses was studied using wet 4% H_2/He as the feed gas. As shown in Fig. 5, the hydrogen fluxes increased with temperature (600–900 °C) for all samples of different thicknesses at a given temperature, hydrogen flux decreased with increasing membrane thickness.

The temperature and thickness dependencies of hydrogen flux of the Ni–BZCY7 cermet membranes were further studied using wet 4% H_2/He as the feed gas. The results are shown in Fig. 6 for membranes with thicknesses ranging from 250 to 1000 μm. The characteristic thickness, defined as $L_c = D^*/k$, where k is the surface exchange coefficient, and D^* is the tracer diffusion coefficient, determines the transition from bulk-diffusion-limited to surface-exchange-rate-limited transport. Over the entire range of thicknesses, the hydrogen flux

Fig. 3. The dependence of hydrogen flux of 266-μm-thick Ni–BZCY7 membrane on the difference between square root of hydrogen partial pressure in feed gas and sweep gas at 900 °C. "f" and "s" stand for feed gas and sweep gas, respectively.
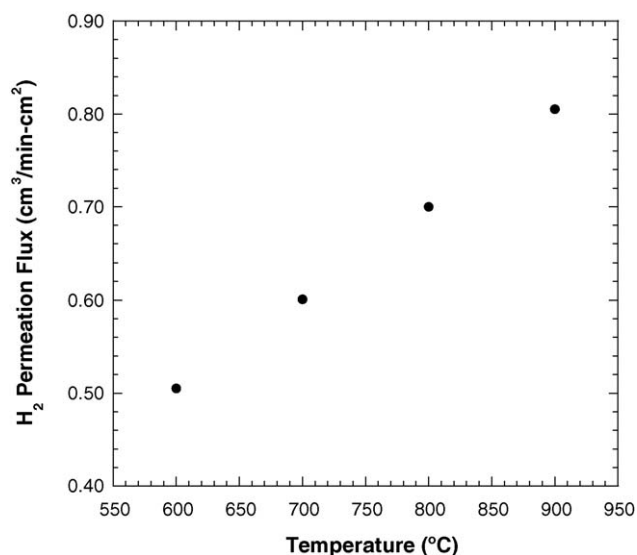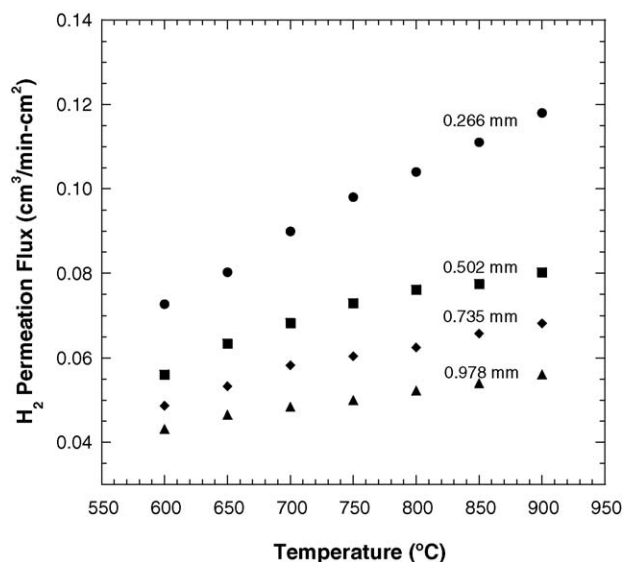

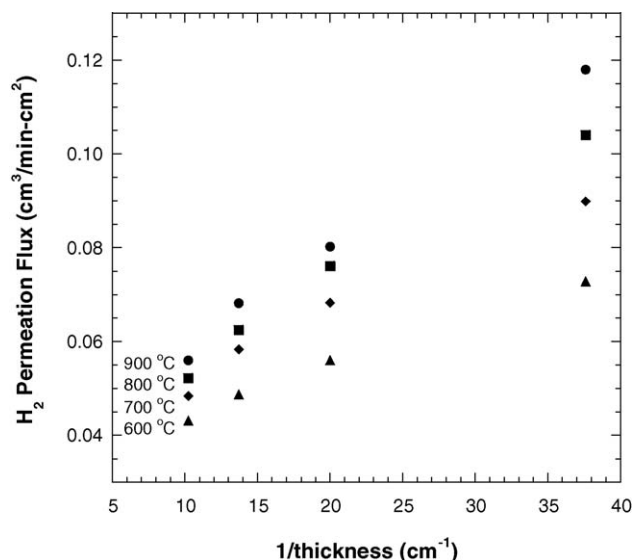Fig. 5. Hydrogen flux through Ni–BZCY7 membranes with different thickness using wet 4% H_2 (balance He) as feed gas.

Fig. 6. Hydrogen flux through Ni–BZCY7 membranes as a function of thickness from 600 to 900 °C using wet 4% H_2 (balance He) as feed gas.

Fig. 7. Time dependence of hydrogen flux through 266-μm-thick Ni–BZCY7 membrane in feed gas of wet x% CO_2 (x = 10, 20, 30, balance 40% H_2/He) at 900 °C.

through the membranes increased with the inverse of membrane thickness in the temperatures range from 600 to 900 °C, indicating that we are still above the characteristic thickness and bulk diffusion kinetics is the rate limiting step in the membranes investigated. However, Fig. 6 does not show clear linear relationship, as it deviates from linearity at reduced thicknesses. Therefore, it is in the mixed control regime (both bulk diffusion and surface exchange kinetics) rather than the pure bulk diffusion controlled regime. The highest flux (0.118 cm^3 min^{-1} cm^2) was measured for a 266-μm-thick membrane at 900 °C. Although interfacial reactions are expected to become important at thinner membranes, these results suggest that the higher hydrogen flux might be achieved by further reducing the membrane thickness.

3.2. Stability study of Ni–BZCY7 cermet membrane

The chemical stability of hydrogen separation membranes is a critical issue, because they will be operated at elevated temperatures in atmospheres containing CO, CO_2, and H_2O among other constituents. To test the stability of Ni–BZCY7 cermet membranes in wet CO_2-containing atmospheres, we monitored the hydrogen flux through the membranes as a function of time upon exposure to varying concentrations of CO_2 gas at 900 °C. The leakage rate of hydrogen was determined by measuring the helium concentration in the sweep gas. Fig. 7 shows the time dependence of the hydrogen flux through a 266-μm-thick Ni–BZCY7 cermet membrane tested using wet feed gas that contained 10, 20, or 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 ultra-high-purity H_2 and He with CO_2. Before and after each stability measurement with a given CO_2 concentration, the UHP H_2 and He were mixed to give the hydrogen concentration (40% H_2) that the wet CO_2-containing gas would subsequently contain. After measurement of the initial hydrogen flux in 40% H_2/He, a given CO_2 con-
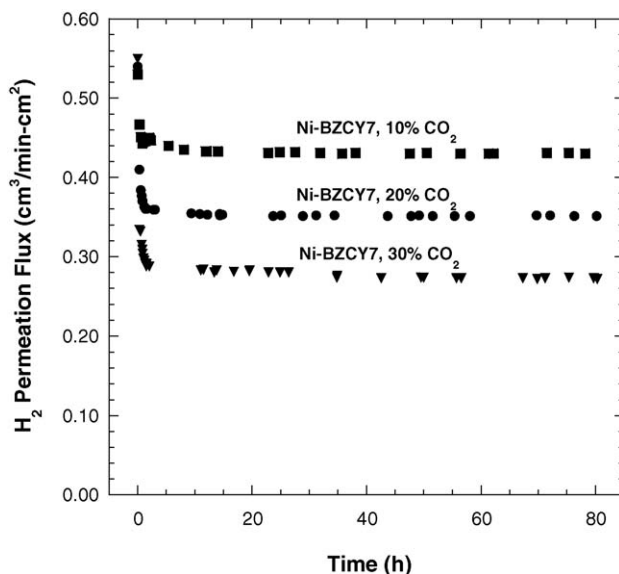
centration was introduced into reactor. The hydrogen flux was found to decrease moderately in the first several hours of exposure after switched to each given CO_2 concentration gas mixer. The initial flux drops increased from ~20 to ~50% as the CO_2 content increased from 10 to 30%, but after this initial decrease, the hydrogen fluxes were stable for 80 h in atmospheres containing up to 30% CO_2. And after the stability study in each given CO_2 concentration gas, the permeation flux was recovered back to the initial flux when switched the feed gas back to H_2/He. By comparing with the unstable performance of Ni–BCY20 cermet membrane in the CO_2 containing atmospheres [12], which the flux continued to decrease at longer exposure in a 20% CO_2 containing atmosphere, this preliminary result indicates that the Ni–BZCY7 cermet membrane has better chemistry stability than the Ni–BCY20 cermet membrane in CO_2 and H_2O-containing atmospheres, and might be suitable for practical applications.

4. Summary

The hydrogen flux through a Ni–BZCY7 cermet membrane increased with temperature under both dry and wet conditions. The fact of increasing hydrogen flux by adding moisture to the feed gas or increasing the hydrogen partial pressure gradient across the membrane implies that the hydrogen flux through the Ni–BZCY7 cermet membrane is limited by the proton transport through the ceramic BZCY7 phase. The dependence of hydrogen flux on membrane thickness indicates that the flux is limited by the bulk diffusion of hydrogen through the ceramic phase over the range of thicknesses that were studied (0.25–1.0 mm). Although interfacial reactions are expected to become important for thinner membranes, these results suggest that we can further increase the hydrogen flux by decreasing the membrane thickness.

The Ni–BZCY7 cermet membrane display relatively high hydrogen permeability and good chemical stability in CO_2 and

H_2O-containing atmospheres. The highest measured hydrogen flux was $0.805\,cm^3\,min^{-1}\,cm^2$ for a dense 266-μm-thick membrane at 900 °C using 100% H_2 as the feed gas. The hydrogen fluxes through membrane were stable, after a small initial decrease, for 80 h in atmospheres containing up to 30% CO_2 at 900 °C, implying that Ni–BZCY7 membranes might be suitable for practical applications.

The permeability and the chemical stability of $Ba(Zr_{0.8-x}Ce_xY_{0.2})O_3$ in wet CO_2 atmospheres will be further improved by adjusting the stoichiometry.

Acknowledgments

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