LETTER

Hydrogen Permeation Performance of Ni-BaZr$_{0.1}$Ce$_{0.7}$O$_{3-\delta}$ Metal-Ceramic Hollow Fiber Membrane

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A dense Ni-BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{3-\delta}$ (BZCY) cermet hollow fiber is fabricated by sintering NiO-BZCY hollow fiber precursors prepared by phase inversion method in 5%H$_2$/95%Ar and its hydrogen permeation performance is investigated. The Ni-BZCY hollow fiber membrane possesses a “sandwich” structure. Finger-like structures are observed near both the inner and outer surfaces, while a dense layer is present in the center part. With 200 mL/min wet 20%H$_2$/80%N$_2$ on the shell side and 150 mL/min high purity Ar on the core side, the hydrogen permeation flux through the Ni-BZCY hollow fiber membrane at 900 °C is 0.53 μmol/cm$^2$·s. Owing to a high packing density, the hydrogen permeation flux per unit volume is greatly improved and membrane components composed of an assembly of hollow fibers may be applied in industrial hydrogen separation.

**Key words:** Hollow fiber, Cermet, Hydrogen permeation, Phase inversion

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About 80% of the world energy demand is currently met by fossil fuels [1, 2]. Because of issues such as energy security, global climate change and local air pollution, hydrogen becomes more attractive as an energy vector and fuel [3]. Unlike fossil fuels, using hydrogen as an energy source produces the only byproduct of water. Moreover, hydrogen is the most abundant element in the universe and possesses the highest energy content per unit weight compared with other fuels [1]. Hydrogen is usually obtained by coal gasification, methane partial oxidation, reforming, or water-gas shift reactions with many byproducts [4]. The separation of hydrogen from other less desirable gases is an important aspect of hydrogen production. Membrane-related separation processes are considered to be more cost-effective than traditional gas separation technologies such as pressure swing adsorption and cryogenic distillation. This is due to the low energy consumption, the continuous operation possibility they offer, the dramatically lower investment cost in plant and the ease of operation [1, 2].

Due to the high cost and the possible embrittlement of palladium-based membranes [5], dense ceramic membranes fabricated from mixed electronic and protonic conductors have been developed. Electrodes or external electrical circuit are not necessary and the membrane uses the hydrogen chemical potential gradient as the driving force for the transportation of hydrogen. Therefore a simple hydrogen separator can be constructed [6]. It has been reported that dense cermet membranes composed of the electronic conductor nickel and the protonic conductor BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{3-\delta}$ (BZCY) display a relatively high hydrogen permeability and good chemical stability in CO$_2$, H$_2$O, and H$_2$S-containing atmospheres [7, 8].

In most previous studies, mainly disc-shaped membranes with limited membrane areas have been employed for hydrogen permeation. However, their low hydrogen permeability and the difficulty of sealing them at high temperatures limit their practical application. Recently, ceramic hollow fiber membranes prepared by an immersion-induced phase inversion technique have been widely used for oxygen separation because of the thinner walls and higher specific surface [9, 10]. However, there have been few investigations of Ni-BZCY composite hollow fiber for hydrogen permeation.

Considering that a more uniform microstructure would result in higher hydrogen permeation flux [11], in this work, NiO-BZCY composite powders were prepared by a one-step nitrate-citric method. By sintering NiO-BZCY hollow fiber precursors in reduced atmosphere, a Ni-BZCY cermet hollow fiber was obtained and its microstructure and hydrogen permeation performance were investigated.

Appropriate amounts of reagent-grade Y$_2$O$_3$, Ni(NO$_3$)$_2$·6H$_2$O, Ce(NO$_3$)$_3$·6H$_2$O, Zr(NO$_3$)$_4$·5H$_2$O,
were weighed and dissolved in nitric acid solution (~8.0 mol/L). Then a stoichiometric amount of BaCO$_3$ was slowly added to the solution under stirring. Subsequently, citric acid was added with a molar ratio of citric acid to metal ions of 1.5:1.0 and the pH value was adjusted to about 8.0 using ammonia solution. The solution was continuously stirred at about 80 °C until it became viscous sol, and then was heated in a furnace until combustion. Finally, the obtained powder was calcined at 1000 °C in air for 3 h.

The NiO-BZCY hollow fiber precursor was prepared using the phase inversion technique. A polymer solution was prepared by dissolving polyethersulfone (PESf, Radel A-100, Solvay Advanced Polymers, L.L.C.) and polyvinylpyrrolidone (PVP, K30, CP, SCRC, China) in N-methyl-2-pyrrolidone (NMP, CP, SCRC, China). Then the as-prepared NiO-BZCY composite powders were slowly added and the mixture was stirred using a planetary ball mill for about two days to ensure uniform distribution of the particles. Extrusion was carried out through a tube-in-orifice spinneret with the outer diameter/inner diameter of 2.6/1.0 mm. Tap water was used as both the internal and external coagulants for all spinning runs. The hollow-fiber precursors were then immersed in water for one day to ensure a complete solidification process. Subsequently, the as-prepared hollow fiber precursors were sintered at 1380 °C for 5 h in a 5%H$_2$/95%Ar environment. During the sintering process, NiO was reduced to Ni and a Ni-BZCY cermet hollow fiber membrane was obtained. A sintered hollow fiber, plugged with epoxy resin at one end and connected to pressurized H$_2$ (0.2 MPa) at the other end, was immersed in a water bath. The gas tightness of the hollow fiber was checked by observing whether any bubble appeared or not. The phase composition was checked using X-ray diffraction (XRD, Philips X’Pert Pro Super, The Netherlands, Cu K$_\alpha$) patterns. The microstructure was examined using a scanning electron microscope (SEM JSM-6700F, JEOL, and Japan) coupled with an energy dispersive X-ray spectroscopy (EDX).

The hydrogen permeation through the Ni-BZCY hollow fiber membrane was measured by feeding a wet 20%H$_2$/80%N$_2$ to the shell side and sweeping the core side with high purity Ar. The effluent gas compositions were analyzed by an online gas chromatograph (GC-14C, Shimadzu) using high purity Ar as the carrier gas. Hydrogen leakage rate through the glass sealant was corrected by measuring the nitrogen concentration in the permeate stream.

Figure 1 shows the XRD patterns of the NiO-BZCY composite powder and the Ni-BZCY hollow fiber. The composite powder consists of NiO and BZCY oxides, and no other diffraction peaks are detected. However, small amounts of BaCO$_3$ and Y-CeO$_3$ oxides are found in the Ni-BZCY hollow fiber membrane. In the sintering process, the reduction of NiO produced a lot of water vapor, while the decomposition of the organic binder and solvent produced large amounts of CO$_2$. The reaction between BZCY, H$_2$O and CO$_2$ may generate BaCO$_3$ and Y-CeO$_3$ oxides.

Figure 2 shows the SEM micrographs and EDX spectra of the Ni-BZCY hollow fiber. The outer diameter and wall thickness of the hollow fiber are about 1.38 and 0.15 mm, respectively. The hollow fiber membrane has a “sandwich” structure: finger-like structures are formed near both the inner and outer walls, while a dense layer is present at the center of the fiber. This asymmetric structure may be attributed to the different precipitation rates within the hollow fiber precursors that occurred during the spinning process [12]. In addition, it can be clearly seen that the membrane is mainly composed of two phases. EDX analysis results indicate that the dark conglubation and the white region are Ni and BZCY phases, respectively. The minor metal Ni is uniformly distributed in the BZCY ceramic matrix.

Figure 3 shows the hydrogen permeation flux $J_{H_2}$ and the outlet hydrogen partial pressure as a function of the feed $F_f$ and sweep $F_s$ gas flow rates. The hydrogen permeation flux and the outlet hydrogen partial pressure both increase with the feed gas flow rate raised. These results demonstrate that the external mass transport of hydrogen to the membrane surface is a limit step for the hydrogen permeation [9]. As the sweep gas flow rate increases, the hydrogen partial pressure on the core side decreases, from 1.3 kPa to 0.4 kPa as the Ar flow rate increases from 25 mL/min to 150 mL/min. The reduction in the hydrogen partial pressure on the permeated side provides a greater driving force and leads to the increase in the hydrogen permeation flux from 0.26 µmol/cm$^2$/s to 0.53 µmol/cm$^2$/s.

Figure 4 presents the temperature dependence of the hydrogen permeation flux. The hydrogen permeation flux increases with increasing temperature. When the wet 20%H$_2$/80%N$_2$ feed gas and Ar sweep gas flow rates are 200 and 50 mL/min, respectively, the hydrogen per-
Ni-BaZr$_{0.7}$Ce$_{0.8}$Y$_{0.2}$O$_{3-\delta}$ Metal-Ceramic

![SEM and EDX spectra of the Ni-BZCY hollow fiber.](image)

**FIG. 2** SEM and EDX spectra of the Ni-BZCY hollow fiber. (a) Cross-section (secondary electron), (b) cross-section near outside surface (backscattered electron), (c) cross-section near inside surface (backscattered electron), (d) EDX spectra of the Ni-BZCY hollow fiber of dark conglobation, (e) EDX spectra of the Ni-BZCY hollow fiber of white region.

![Hydrogen permeation flux](image)

**FIG. 3** Hydrogen permeation flux $J_{H_2}$ and outlet hydrogen partial pressure as a function of the feed $F_f$ (a) and sweep $F_s$ (b) gas flow rates at 900 °C.

The hydrogen permeation flux reaches 0.37 μmol/cm$^2$·s at 900 °C. The hydrogen permeation flux of a 1-mm-thick Ni-BZCY membrane at 900 °C is about 42 nmol/cm$^2$·s [11]. For BaCe$_{0.8}$Y$_{0.2}$O$_3$ (BCY) with high proton conductivity, the hydrogen flux through the Ni-BCY membranes with 0.08 mm thicknesses in 3.8%H$_2$/96.2%He feed mixture is about 0.18 μmol/cm$^2$·s [13]. Although the hydrogen permeability is studied under different conditions, the hydrogen permeability of the hollow fiber membrane is superior to the disc-shaped membrane. In addition, the plate module typically has a membrane packing density of several tens m$^2$/m$^3$ whereas hollow fiber modules can reach several thousand m$^2$/m$^3$. Therefore, the hydrogen permeation per unit volume is greatly improved and membrane separators assembled from hollow fibers have the potential for industrial applications.

In conclusion, NiO-BZCY composite powders were prepared by a one-step nitrate-citric method. NiO-BZCY hollow fiber precursors prepared by an immersion-induced phase inversion technique were sintered in a reduced atmosphere to obtain a Ni-BZCY cermet membrane. The cermet hollow fiber has a “sandwich” structure: finger-like structures near both the inner and outer walls, but a dense layer in the middle of the fiber. The hydrogen permeation performance of the cermet hollow fiber increases with...
FIG. 4 Temperature dependence of the hydrogen permeation flux. Ar flow rate on the core side: 50 mL/min, 20%H₂/80%N₂ flow rate on the shell side: 200 mL/min.

rising temperature and feed and sweep gas flow rates. Since the wall thickness is very small, the hydrogen permeation flux reaches 0.53 μmol/cm²s at 900 °C using 200 mL/min 20%H₂/80%N₂ and 150 mL/min Ar as the feed and sweep gas, respectively, which is significantly higher than that of a disc-shaped membrane with a high relative thickness.

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