Ni-$BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ high flux CO_2-tolerant hydrogen permeation membrane

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As an important raw material in chemical and refining industries, hydrogen is consumed in enormous quantity to synthesize ammonia, methanol, liquid hydrocarbons, etc. Achieving cost-effective and large-scale hydrogen production with feasible CO_2 sequestration has significant economic benefits and contributes to a cleaner environment. In the near future, most hydrogen will still be produced from fossil fuels, especially through steam reforming of natural gas (methane). Consequently, separation of hydrogen from the reformate stream is a crucial step in the mass production of pure hydrogen. High purity hydrogen can be directly obtained via the permeation of hydrogen through membrane under pressure gradient at high temperature. Comparing with the prevailing pressure swing adsorption (PSA) method, separation of hydrogen through a hydrogen permeation membrane is simple and cost-effective. Furthermore, nearly all the carbon species is retained in a high pressure CO_2 stream advantageous for sequestration. Composite membranes consisting of a solid-state proton conductor and an electronic conductor (e.g., nickel) are designed for this application.

Although acceptor-doped $BaCeO_3$ shows the highest proton conductivities, it suffers from poor chemical stability in H_2O and CO_2. For example, hydrogen permeation flux of Ni–$BaCe_{0.8}Y_{0.2}O_{3-\delta}$ diminished to zero in 30% CO_2 at 900°C in ~20 h due to the formation of barium carbonate[1]. The chemical stability of $BaCeO_3$ can be improved by doping Zr at the Ce sites, but with the expense of sharp reduction in proton conductivity and sintering activity[2]. Ni–$BaZr_{0.8-x}Ce_xY_{0.2}O_{3-\delta}$ ($0.4 \le x \le 0.7$) membranes showed better chemical stability in CO_2 than Ni–$BaCe_{0.8}Y_{0.2}O_{3-\delta}$ but still suffered serious performance losses during operation. The degradation was attributed to the insulating effect of $BaCO_3$ formed in the reaction between the membrane and CO_2. Recently, Yang et al. have reported that $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) possesses high proton conductivity and high tolerance to CO_2 and H_2S, showing excellent performance as anode materials in solid oxide fuel cells[3]. Therefore, BZCYYb can potentially be a very promising material for hydrogen permeation membrane. Ni-BZCYYb cermet membrane was fabricated and its permeation behavior in CO_2-containing feed gas was investigated.

Surprisingly, in many cases, the hydrogen permeation fluxes increased rather than decreased when CO_2 was introduced to feed gas, which cannot be explained by the generally-accepted perovskite and CO_2 reaction mechanism. This singular behavior inspires a detailed investigation on the mechanism, which can provide guidance on the development of CO_2-resistant hydrogen permeation membrane.

BCZYYb powder was synthesized by sol-gel combustion method and calcined at 1100°C for 5h. Ni powder and BCZYYb powder were mixed in volume ratio of 40:60. The mixed powder was uniaxially pressed and sintered at 1440°C for 10 h in 4% H_2/N_2 to obtain Ni-BCZYYb membrane. The membrane was tested in a customer-built set-up for hydrogen permeability measurements.

Fig. 1 shows the hydrogen permeation behavior of Ni-BZCYY membrane with and without CO_2 in the feed gas stream. In dry feed gas, when N_2 was replaced by CO_2, the hydrogen permeation fluxes increased by 2 times. In wet feed gas, the hydrogen permeation flux was also improved, but in less magnitude compared with that in dry hydrogen stream. Analysis of the exhaust feed gas showed considerable amount of CO and H_2O formation after CO_2 was introduced, accompanied by the decrease of H_2 concentration.

The improvement of hydrogen permeation fluxes was ascribed to the increase of moisture content in feed gas, which acutely enhanced the proton conductivity of BZCYYb and hydrogen permeation flux of the membrane, especially in dry feed gas.

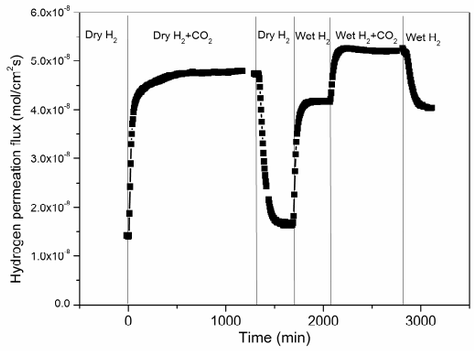

Fig. 1 Hydrogen permeation behavior of a 0.9-mm-thick Ni-BZCYYb membrane at 900°C when CO_2 was introduced and removed from the feed gas. Feed gas: 20 mL/min H_2, 47/50 mL/min He (dry or wet condition, respectively), 30 mL/min N_2/CO_2. Sweep gas: 20 mL/min N_2.

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