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Hydrogen separation by dense cermet membranes

U. Balachandran *, T.H. Lee [1], L. Chen [2], S.J. Song [3], J.J. Picciolo [4], S.E. Dorris [5]

Energy Technology Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439-4838, USA

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Abstract

Novel cermet (i.e. ceramic–metal composite) membranes have been developed to separate hydrogen from mixed gases, particularly product streams generated during coal gasification and/or methane reforming. Hydrogen separation with these membranes is non-galvanic, i.e. it does not use electrodes or an external power supply to drive the separation, and hydrogen selectivity is nearly 100% because the membranes contain no interconnected porosity. The hydrogen permeation rate has been measured as a function of temperature (500–900 °C), membrane thickness ($\approx$22–210 μm), and partial pressure of hydrogen (0.04–1.0 atm) in the feed gas. The hydrogen flux varied linearly with the inverse of membrane thickness, and reached $\approx$20 cm^3(STP)/min cm^2 for a membrane with a thickness of $\approx$22 μm at 900 °C with 100% H_2 (at ambient pressure) as the feed gas. The results indicate that the hydrogen flux is limited by bulk diffusion and might be higher for a thinner ($<$22 μm) membrane. Some of the membranes were tested in a simulated syngas mixture containing H_2, CO, CO_2, and CH_4, and showed no degradation in performance. Hydrogen flux measurements made in H_2S-containing atmospheres for times approaching $\approx$270 h showed that a 200-μm-thick cermet membrane was stable in gases containing up to $\approx$400 ppm H_2S. While longer-term studies are needed, these results suggest that the cermet membranes may be suitable for practical hydrogen separation applications.

Keywords: Dense membranes; Cermet; Hydrogen permeation

1. Introduction

As part of the effort to devise cost-effective, efficient processes for producing and utilizing hydrogen, Argonne National Laboratory (ANL) is developing dense hydrogen-permeable membranes for separating hydrogen from mixed gases at commercially significant fluxes under industrially relevant operating conditions. Product streams that are generated during coal gasification, methane partial oxidation, and water–gas shift reactions are of particular interest in this work. To maintain simplicity in design, fabrication, and operation, while minimizing operating costs, membranes will ideally operate in a non-galvanic mode (i.e. their operation will not involve electrodes or electrical circuitry). This will require membrane materials with suitable electronic and protonic conductivities as well as high hydrogen solubility and diffusivity. In addition, the fabricated materials must be thin and dense to maximize the hydrogen flux and maintain high hydrogen selectivity.

The membrane development effort at ANL initially focused on $BaCe_{0.8}Y_{0.2}O_{3-\delta}$ (BCY), a mixed proton/electron conductor whose high total electrical conductivity [1,2] suggested that it might yield a high hydrogen flux without using electrodes or external electrical circuitry. Early results showed, however, that BCY's electronic component of conductivity is insufficient to allow a high non-galvanic hydrogen flux [3,4]. To increase the electronic conductivity, and thereby increase the hydrogen flux, we developed various cermet membranes, in which 40–50 vol% of a metal (or alloy) is dispersed in a ceramic matrix [5,6]. In these cermet membranes, the metal enhances the hydrogen permeability of the ceramic phase by increasing the electronic conductivity of the composite. If the metal (or alloy) has high hydrogen permeability (e.g. Pd, Pd–Ag, Pd–Cu, Nb, Ta, Zr, etc.), it is called a hydrogen transport metal, and it provides an additional transport path for hydrogen. A cermet membrane that contains a hydrogen transport metal in a thermodynamically and mechanically stable ceramic matrix, e.g. Al_2O_3 or ZrO_2, presently exhibits the highest hydrogen flux

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* Corresponding author. Tel.: +1 630 252 4250; fax: +1 630 252 3604.
E-mail addresses: balu@anl.gov (U. Balachandran), thlee@anl.gov (T.H. Lee), ling.chen@anl.gov (L. Chen), song@anl.gov (S.J. Song), picciolo@anl.gov (J.J. Picciolo), dorris@anl.gov (S.E. Dorris).
[1] Tel.: +1 630 252 5374; fax: +1 630 252 3604.
[2] Tel.: +1 630 252 4193; fax: +1 630 252 3604.
[3] Tel.: +1 630 252 7761; fax: +1 630 252 3604.
[4] Tel.: +1 630 252 6233; fax: +1 630 252 3604.
[5] Tel.: +1 630 252 5084; fax: +1 630 252 3604.

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[≈20 cm^3(STP)/min cm^2], and functions well as a hydrogen separation membrane.

In this paper, we report hydrogen flux measurements for Pd/YSZ membranes as a function of temperature, partial pressure of hydrogen in the feed stream, and membrane thickness. Also, because hydrogen separation membranes are expected to contact gas streams that contain CO, CO_2, CH_4, and H_2S, in addition to H_2, the stability of membranes in mixed-gas streams is an important issue. We report here the hydrogen flux of cermet membranes versus time during exposure to feed gases containing H_2, CO, CO_2, CH_4, and H_2S.

2. Experimental

The powder mixture for fabricating the cermet membranes was prepared by mechanically mixing 50 vol% Pd (average particle size ≈1.5 μm) with Y_2O_3-stabilized ZrO_2 (i.e. YSZ) having an average particle size of ≈1.0 μm. The powder mixture was pressed into disks, which were then sintered in air at 1400–1500 °C for 5–10 h. For hydrogen permeation 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. Membrane thickness was measured using a micrometer, and ranged from ≈22–200 μm. Thickness was also measured by scanning electron microscopy (SEM) for membranes whose microstructures were examined after the permeation tests were concluded. Polished cermet membranes were affixed to one end of an alumina tube using a gold gasket for a seal, as illustrated in Fig. 1. Although polishing the 22-μm-thick membrane required extra care, and the resulting membrane was more fragile than thicker samples, all the samples were sufficiently robust to be tested using the fixture shown in Fig. 1. In order to measure the hydrogen permeation rate (i.e. hydrogen flux), the alumina tube was inserted into a furnace with a sealed membrane and the associated gas flow tubes. Feed gases included various concentrations of hydrogen in helium, 100% H_2, simulated synthesis gas (61.3% H_2, 8.2% CH_4, 11.5% CO, 9.0% CO_2, 10% He), and gases with up to 2922 ppm H_2S.

The stability of Pd/YSZ membranes in H_2S-containing atmospheres was determined by measuring the hydrogen flux versus time in atmospheres with progressively higher H_2S concentrations. Gas mixtures for these tests were prepared using mass flow controllers to blend ultrahigh purity He with H_2 and/or synthesis gas that contained known H_2S concentrations. Permeated hydrogen was carried away by an inert sweep gas and analyzed using a Hewlett-Packard 6890 gas chromatograph with a thermal conductivity detector. Because we perform separate studies using cermet membranes that contain Ni, which can be oxidized by O_2 or H_2O impurities in the sweep gas, the sweep gas (N_2) contained 100 ppm H_2 to prevent oxidation of Ni. The same sweep gas was used in the present study, because the small concentration of H_2 (100 ppm) was negligible compared to the permeated H_2. Gas leakage through the sample and/or seal was routinely tested by measuring the helium concentration in the sweep gas; typical leakage was about 5% of the measured total hydrogen flux. The hydrogen flux through the cermet membranes was calculated by subtracting the leakage from the measured hydrogen in the sweep side. Samples were examined after exposures to H_2S-containing gases using a JEOL-JSM 5400 SEM, and the chemical compositions of various features were determined by energy dispersive spectroscopy (EDS) using a Noran Voyager X-ray analyzer.

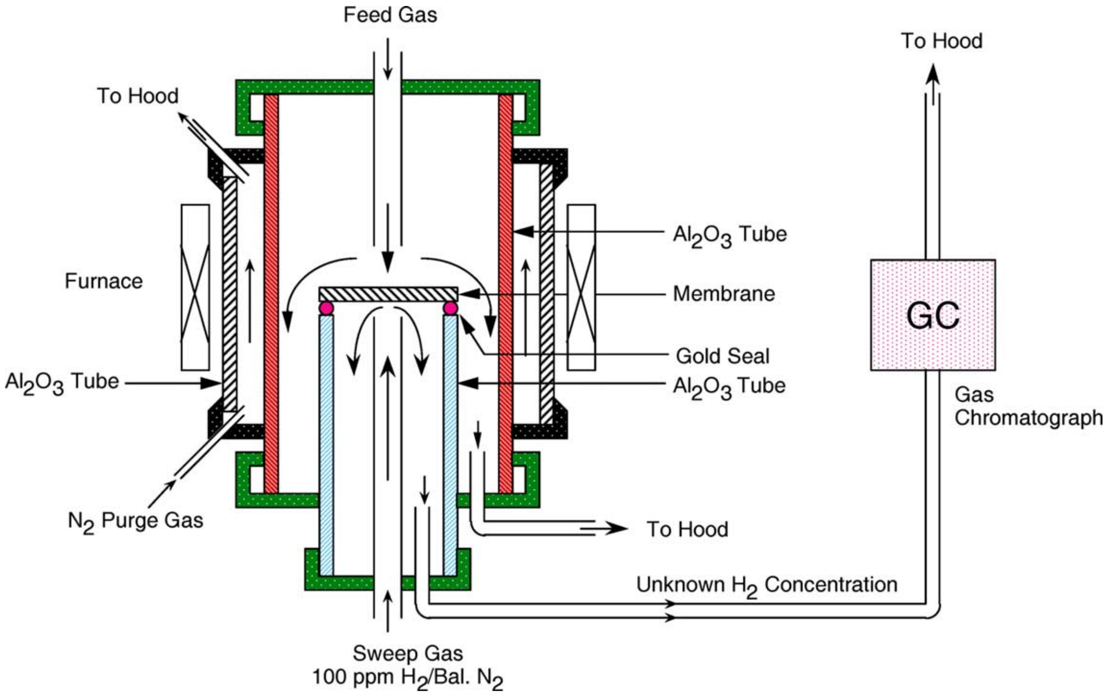

Fig. 1. Schematic illustration of set-up used to measure hydrogen flux through cermet membranes.