



Dense cermet membranes for hydrogen separation[☆]



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ABSTRACT

Dense cermet (i.e., ceramic–metal composite) membranes have been developed for separating hydrogen from mixed gases, particularly product streams generated during coal gasification and/or steam methane reforming. Hydrogen separation with these membranes yields high-purity hydrogen, thereby eliminating the need for post-separation purification steps. Extensive tests have been conducted with cermet membranes made by mixing ≈ 50 – 60 vol.% Pd with Y_2O_3 -stabilized ZrO_2 . Using several feed gas mixtures, the hydrogen permeation rate, or flux, for the membranes was measured in the temperature range 400–900 °C. With pure hydrogen at ambient pressure as feed gas, an ≈ 18 - μm -thick membrane on a porous substrate gave a measured flux of ≈ 26 cm³[STP]/min-cm² at 400 °C and ≈ 52 cm³[STP]/min-cm² at 900 °C. We also measured the hydrogen flux through a thicker (≈ 150 μm) membrane at 400 °C using a mixture of H₂, CO, CO₂, H₂O, and He at ≈ 200 psig as feed gas. Hydrogen flux measurements in H₂S-containing atmospheres showed that the cermet membranes are stable at 900 °C in gases that contain $\approx 80\%$ H₂/400 ppm H₂S. Because formation of palladium sulfide (Pd₄S) can seriously degrade hydrogen permeation through Pd-containing cermet membranes, the Pd/Pd₄S stability phase boundary of the cermet membrane was determined in the temperature range 450–650 °C using various feed gases that contained 10–73% H₂ and 8–400 ppm H₂S. Given these promising results, longer studies using real-world coal gasification conditions should be pursued.

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1. Introduction

The Office of Fossil Energy (FE) at the U.S. Department of Energy (DOE) sponsors a wide range of research, development, and demonstration programs to maximize the use of the vast domestic fossil resources and to ensure a fuel-diverse energy sector while responding to global environmental concerns. Cost-effective, membrane-based reactor and separation technologies are of considerable interest to DOE's clean coal program to develop advanced coal-based power and fuel technologies. Argonne National Laboratory is developing dense hydrogen transport membranes (HTMs) for separating hydrogen from mixed gases, particularly product streams generated during coal gasification and/or methane reforming. Hydrogen separation with these membranes is nongalvanic (i.e., it does not use electrodes or an external power supply to drive

the separation), and hydrogen separated from the feed stream is of high purity, so post-separation purification steps are unnecessary.

Materials development for the HTM at Argonne has followed a three-pronged approach. In one approach, we investigated single-phase mixed (ionic/electronic) conducting perovskite ceramics [1,2]. The single-phase membranes gave a low hydrogen flux due to their poor electronic conductivity [3,4]. In our second approach, we developed cermet (i.e., ceramic–metal composite) membranes that contained mixed-conducting perovskite ceramics combined with a metallic component [5–9]. In these cermets, the metal enhanced the hydrogen flux of the ceramic phase by increasing the electronic conductivity of the cermet. In our third approach, we dispersed a hydrogen transport metal, i.e., metal with high hydrogen permeability (Pd, Pd–Ag), in a thermodynamically and mechanically stable ceramic matrix (Al₂O₃ or yttria-stabilized ZrO₂, YSZ) [10]. The cermets, made by our third approach, exhibit the highest hydrogen flux [11,12].

In this paper, we report hydrogen flux measurements for Pd/YSZ cermet membranes as a function of temperature. Good chemical stability is a critical requirement for HTMs due to the corrosive nature of product streams from coal gasification and/or methane reforming. Hydrogen sulfide (H₂S) is a particularly corrosive contaminant that HTMs are expected to encounter. When H₂S reacts with a Pd/YSZ cermet membrane, palladium sulfide (Pd₄S) forms on the membrane surface. Because Pd₄S impedes hydrogen

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permeation through the membrane, the chemical stability of HTMs was evaluated by determining the conditions under which Pd₄S forms. The Pd/Pd₄S phase boundary was determined in the temperature range ≈ 450 – 650 °C using various feed gases that contained 10–73% H₂ and ≈ 8 –400 ppm H₂S. To assess the effect of water vapor on hydrogen permeation through HTMs, the chemical stability of the cermet membrane was tested in the presence of steam by measuring its hydrogen flux in feed gas that contained 0.03–0.49 atm H₂O. Finally, we report here the hydrogen flux of the cermet membrane versus time (up to 120 days) during exposure to simulated syngas containing H₂, CO, CO₂, and H₂O. In addition, it is anticipated that the cermet-type membranes can overcome some drawbacks of pure Pd or Pd alloy membranes, i.e., reduce the cost and improve the mechanical strength of the membrane at high temperature (>700 °C).

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 Y₂O₃-stabilized ZrO₂ (average particle size, ≈ 1.0 μm). This powder mixture was pressed into disks and sintered at ≈ 1400 °C for ≈ 5 h in ambient air. For hydrogen permeation tests, both sides of the disks were polished with 600-grit SiC paper to obtain the desired thickness and produce faces that were flat and parallel to one another. Thin films of cermet membrane on porous substrates were prepared by a paste-painting method, in which the cermet powders were mixed in a solution of α -terpineol and isopropyl alcohol with polyvinyl butyral as a binder and dibutyl phthalate as a plasticizer. The thin-film cermet layer contained 60 vol.% Pd. Examination of multiple cermet layers after hydrogen flux measurements showed no signs of segregation by Pd and ZrO₂. The concentration of isopropyl alcohol was varied to control the viscosity of the paste. The paste was brushed onto partially sintered alumina substrates, and then the films/substrates were sintered at 1400 °C for ≈ 5 h in ambient air. The hydrogen permeation rate (i.e., hydrogen flux) was measured by a procedure described elsewhere [12]. For hydrogen permeation tests at ambient pressure, the disk-type cermet membranes were affixed to one end of an alumina tube using a gold gasket for a seal. Graphite washers were used to make seals for tests at high pressure. 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% H₂, simulated synthesis gas, and gases with up to ≈ 3000 ppm H₂S. A small concentration of helium was used in the feed stream in order to constantly monitor the gas leakage through the sample and/or seals.

Permeated hydrogen was carried away by an inert sweep gas and analyzed using a Hewlett–Packard 6890 gas chromatograph with a thermal conductivity detector. For a given condition, the hydrogen concentration in the sweep stream was measured two to four times, and the average of those readings was used to calculate the hydrogen flux. Individual readings varied from the average value by $\leq 10\%$. 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. Membrane microstructures and thickness were measured with a JEOL 5400 scanning electron microscope (SEM). Energy dispersive spectroscopy (EDS) using a Voyager system (Thermo Electron Scientific Instruments Corp.) was employed for chemical analysis of microstructural features.

The Pd/Pd₄S phase boundary was determined in the temperature range ≈ 450 – 650 °C in tests using various feed gases that

contained 10–73% H₂ and ≈ 8 –400 ppm H₂S. Mass flow controllers (MKS 1179A) were used to blend appropriate gases. The total flow rate of the mixture was 200 cm³/min, and the chamber holding the sample had a volume of ≈ 2600 cm³; therefore, a volume of gas equivalent to the volume of the sample chamber flowed in ≈ 13 min, meaning that the gas composition in the sample chamber equaled the expected composition within no more than ≈ 1 h of starting the flow of the gas mixture. The samples were equilibrated by heating at a rate of 180 °C/h in flowing He, and then switching the feed gas mixture when the targeted temperature was reached. After holding the sample at the targeted temperature for 50 h, the gas was switched back to He, and the sample was cooled at a rate of 180 °C/h. The samples were equilibrated for 50 h because this length of time allowed an easily discernible layer of Pd₄S to form if Pd₄S was stable. After each exposure, a cross section of the sample was examined with SEM/EDS to determine whether a layer of Pd₄S had formed or the Pd had been stable during the exposure. If Pd₄S formed during the exposure, a 5- to 10- μm -thick layer was clearly visible on the sample's surface. The stability of Pd/YSZ membranes was also tested in H₂S-containing atmospheres by measuring the hydrogen flux versus time in atmospheres with progressively higher H₂S concentrations.

3. Results and discussion

Fig. 1 shows the temperature dependence of hydrogen flux through an ≈ 18 - μm -thick Pd/YSZ cermet membrane on a porous alumina substrate disk made by the paste-painting method [8]. The feed gas was 90% H₂/He and the sweep gas was N₂. The thickness of the porous alumina substrate was ≈ 1.65 mm. The flow rate of both feed and sweep gas was adjusted to ≈ 500 mL/min to minimize concentration polarization. The feed and sweep gases were at ambient pressure. This membrane gave record high flux values of ≈ 26 cm³ (STP)/min-cm² [≈ 50 ft³ (STP)/h-ft², SCFH/ft²] at 400 °C and ≈ 52 cm³ (STP)/min-cm² [≈ 100 ft³ (STP)/h-ft², SCFH/ft²] at 900 °C. Fig. 2 shows a cross sectional micrograph of the dense cermet membrane on a porous alumina substrate. The influence of the porous alumina substrate was investigated by Park et al. [13], who measured the hydrogen flux of 0.1-mm-thick Pd foil with and without porous alumina substrate in order to assess the magnitude of the substrate's effect. For porous alumina substrate, ≈ 3 wt% carbon lampblack was added to create porosity. It was found that the substrate impeded gas-phase transport of hydrogen

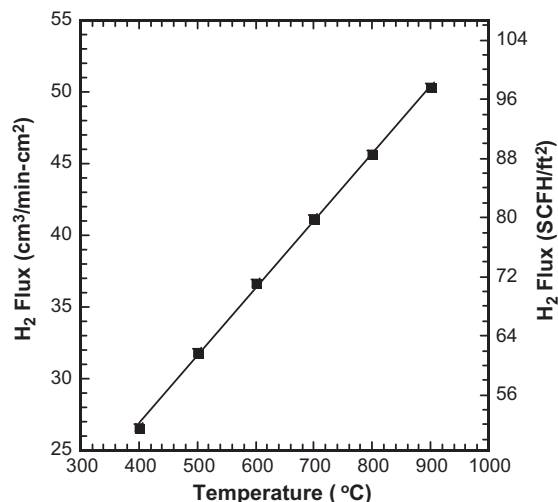


Fig. 1. Hydrogen flux through ≈ 18 - μm -thick cermet membrane on a porous substrate versus temperature using 90% H₂/He at ambient pressure as feed gas.

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