

DEVELOPMENT OF DENSE CERAMIC MEMBRANES FOR  
HYDROGEN SEPARATION\*

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## Development of dense ceramic membranes for hydrogen separation\*

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We developed novel cermet (i.e., ceramic-metal composite) membranes for separating hydrogen from gas mixtures at high temperature and pressure. The hydrogen permeation rate in the temperature range of 600-900°C was determined for three classes of cermet membranes (ANL-1, ANL-2, and ANL-3). Among these membranes, ANL-3 showed the highest hydrogen permeation rate, with a maximum flux of 3.2 cm<sup>3</sup>/min-cm<sup>2</sup> for a 0.23-mm-thick membrane at 900°C. Effects of membrane thickness and hydrogen partial pressure on permeation rate indicated that bulk diffusion of hydrogen is rate-limiting for ANL-3 membranes. The lack of degradation in permeation rate during exposure to a simulated syngas mixture suggests that ANL-3 membranes are chemically stable and suitable for long-term operation.

### 1. INTRODUCTION

The DOE Office of Fossil Energy sponsors a wide variety of research, development, and demonstration programs whose goals are to maximize the use of vast domestic fossil resources and to ensure a fuel-diverse energy sector while responding to global environmental concerns. Development of cost-effective membrane-based reactor and separation technologies is of considerable interest for applications in advanced fossil-based power and fuel technologies. Because concerns over global climate change are driving nations to reduce CO<sub>2</sub> emissions, hydrogen is considered the fuel of choice for the electric power and transportation industries. Although it is likely that renewable energy sources will ultimately be used to generate hydrogen, fossil-fuel-based technologies will supply hydrogen in the interim.

Dense membranes for separating hydrogen from gas mixtures are being developed at Argonne National Laboratory (ANL) and the National Energy Technology Laboratory (NETL). These efforts initially focused on BaCe<sub>0.8</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> (BCY) because its total electrical conductivity is among the highest of known proton conductors [1,2]. However, its electronic

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component of conductivity is insufficient for nongalvanic hydrogen permeation [3,4]. In order to produce membranes with increased electronic conductivity, we made ceramic-metal composite (i.e., cermet) membranes by adding various metals to BCY. Nongalvanic hydrogen permeation was observed in two such membranes (ANL-1 and ANL-2) but the hydrogen flux was much higher in ANL-2 because the hydrogen permeability of its metal was much higher than that of the metal in ANL-1 [5,6]. Based on these results, a third class of cermet membrane (ANL-3) was developed in which the metal phase provides the path for hydrogen diffusion while the ceramic phase acts only as a mechanical support.

This paper describes the present status of cermet membrane development at ANL/NETL. The hydrogen permeation properties are compared for three classes of cermet membranes (ANL-1, -2, and -3), and the effects of membrane thickness, temperature, and hydrogen partial pressure on the permeation flux of ANL-3 are presented. In addition, the long-term chemical stability of ANL-3 membranes in simulated "syngas" is demonstrated.

## 2. EXPERIMENTAL

To prepare ANL-1 and -2 membranes, two different metallic powders were first mixed with BCY powder, whose preparation has been described previously [6]. ANL-3 membranes were prepared by first mixing commercially available  $\text{BaTiO}_3$  (Alfa-Aesar) with a third metal. All three membranes were prepared so as to give 40 vol.% of the metal phase. The powders were mixed with mortar and pestle in isopropyl alcohol, and the alcohol was then evaporated. Pellets were made from the resulting powder mixture by uniaxial pressing at 200 MPa. ANL-1 membranes were sintered at 1400-1420°C for 5 h in 4%  $\text{H}_2$ /balance  $\text{N}_2$ . ANL-2 and -3 membranes were sintered in ambient air for 12 h at 1510 and 1350°C, respectively.

For permeation testing, a sintered disk was polished with 600-grit SiC polishing paper and affixed to an alumina tube with spring-loaded alumina rods. A gold ring between the disk and the alumina tube formed a seal when the assembly was heated at 950°C for 5 h. One side of the membrane was purged with 4%  $\text{H}_2$ /balance He during the sealing procedure, while the other side was purged with 100 ppm  $\text{H}_2$ /balance  $\text{N}_2$  (or Ar). The effective membrane area was  $\approx 1.3 \text{ cm}^2$ .

The apparatus for measuring hydrogen permeation has been described elsewhere [6]. Both sweep ( $\approx 100 \text{ cm}^3/\text{min}$ ) and feed ( $\approx 100 \text{ cm}^3/\text{min}$ ) gases were controlled with MKS 1179A mass flow controllers. A small concentration of hydrogen, 100 ppm, was added to the sweep gas to prevent oxidation of the metal in the membrane and was subtracted in calculating the permeation rate. The gas concentrations in the sweep gas were analyzed with a gas chromatograph (Hewlett-Packard 6890) that was periodically calibrated with standard gases. Hydrogen leakage was corrected by measuring the helium concentration on the sweep side and typically represented  $<10\%$  of the total hydrogen permeation flux.

Both dry and wet feed gas were used. For the wet condition, the feed gas was bubbled through a water bath at room temperature, while the dry feed gas was introduced directly into the furnace from the gas cylinder. Simulated "syngas" consisted of 66%  $\text{H}_2$ , 33% CO, and 1%  $\text{CO}_2$  and was purchased from AGA Gas, Inc.

### 3. RESULTS AND DISCUSSION

Figure 1 compares the hydrogen permeation rates for ANL-1, -2, and -3 membranes, measured by using a feed gas of 4% H<sub>2</sub>/balance He. In each case, the membrane thickness was nearly the same ( $\approx 0.5$  mm) and identical measurement conditions were used, so the permeation rates could be directly compared for the three samples. The permeation rate for ANL-3 was  $\approx 3$  times higher than that of ANL-1 and  $\approx 30$ -50% higher than that of ANL-2 over the whole temperature range. The permeation rate for ANL-3 is higher than that for the other membranes because its metal phase has the highest hydrogen permeability. Due to its higher hydrogen flux, the remainder of the paper focuses on the ANL-3 membrane.

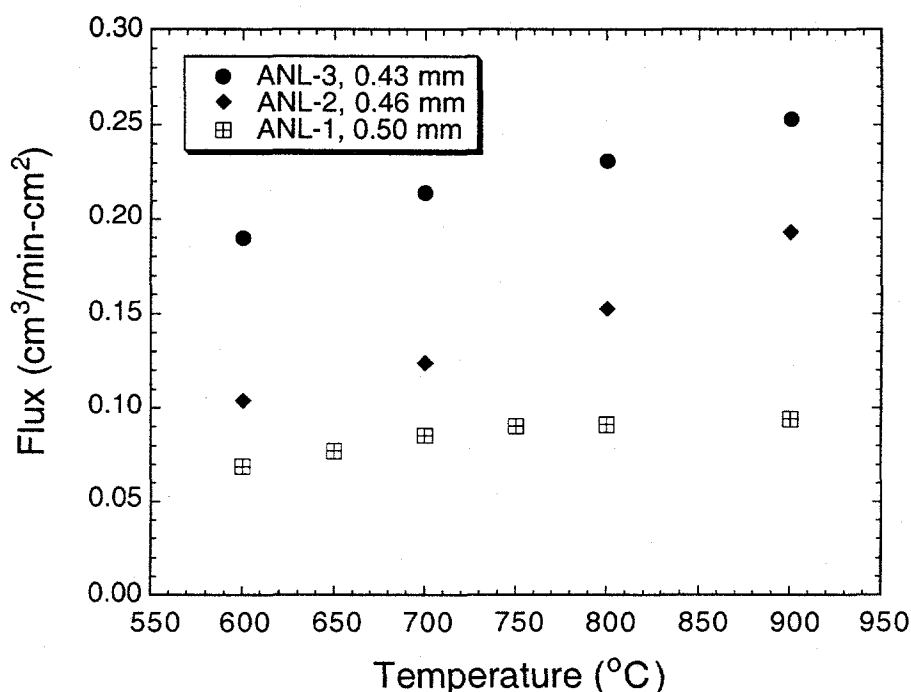


Fig. 1. Hydrogen flux through ANL-1, 2, and -3 membranes with 4% H<sub>2</sub> feed gas.

Figure 2 shows the temperature dependence of hydrogen flux for ANL-3 membranes with thicknesses of 0.23 and 0.43 mm. Measurements were made over a temperature range of 600-900°C using wet 100% H<sub>2</sub> as feed gas and 100 ppm H<sub>2</sub>/balance N<sub>2</sub> as sweep gas. The hydrogen permeation rate increased with temperature and was approximately proportional to the inverse of membrane thickness over the whole temperature range. This suggests that the bulk diffusion of hydrogen is rate-limiting in ANL-3 membranes and that the permeation flux may be increased further by reducing the membrane thickness. A maximum flux of 3.2 cm<sup>3</sup>(STP)/min-cm<sup>2</sup> was measured for the 0.23-mm-thick membrane at 900°C.

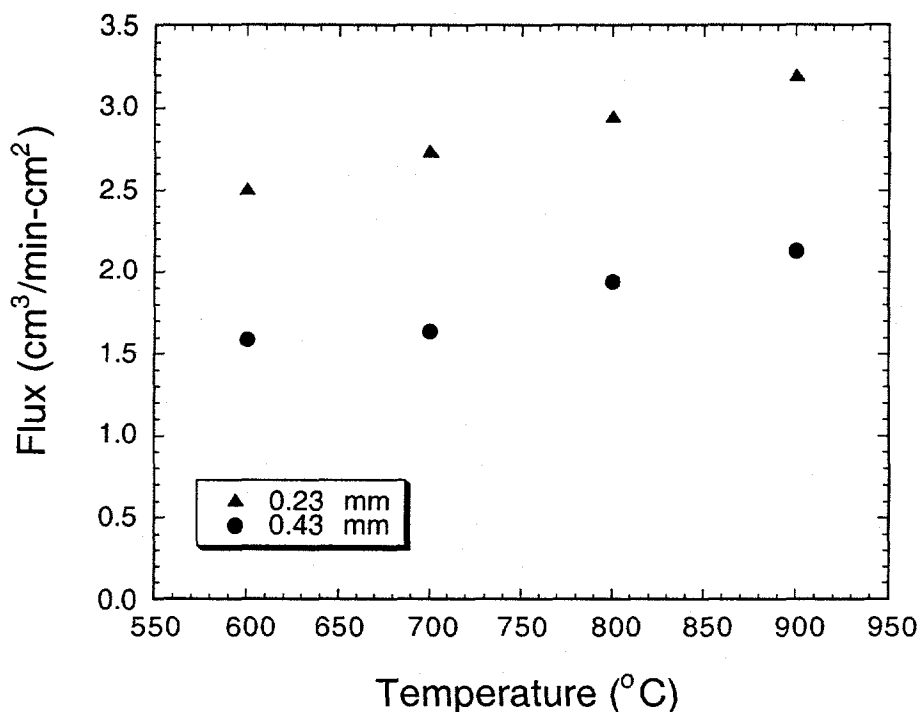


Fig. 2. Hydrogen flux through ANL-3 membranes with wet 100% H<sub>2</sub> as feed gas.

The effect of hydrogen partial pressure on the permeation flux is shown in Fig. 3 for the 0.23-mm-thick ANL-3 membrane. Measurements were performed at 800 and 900°C. Helium and 100% hydrogen (or syngas) were mixed to obtain desired hydrogen partial pressures in the feed gas. The hydrogen permeation flux is plotted as a function of the difference in square root of hydrogen partial pressure for the feed and sweep sides of the membrane. At both temperatures, flux is linear with the difference in square root of hydrogen partial pressure, which is characteristic of bulk-limited hydrogen diffusion through metal membranes [7]. These results are consistent with the thickness dependence of the permeation flux (Fig. 2) and confirm that hydrogen permeation through this ANL-3 membrane is limited by the bulk diffusion of hydrogen in this thickness range. At some lesser thickness, however, interfacial reactions may become rate-limiting.

The chemical stability of an ANL-3 membrane in syngas was tested by measuring its hydrogen permeation at several temperatures for times up to 190 h. The results are shown in Fig. 4 for a 0.43-mm-thick membrane. Before and after syngas measurements at each temperature, 4% H<sub>2</sub>/balance He feed gas was flowed and the leakage rate of hydrogen was estimated by measuring the helium concentration in the sweep gas. During the measurements, no helium leakage was measured at any of the temperatures. As seen in Fig. 4, no noticeable decrease in flux was observed in up to 190 h operation (at 500°C). Likewise, a 0.23-mm-thick ANL-3 membrane showed no decrease in flux during 120 h of exposure to syngas at 900°C.

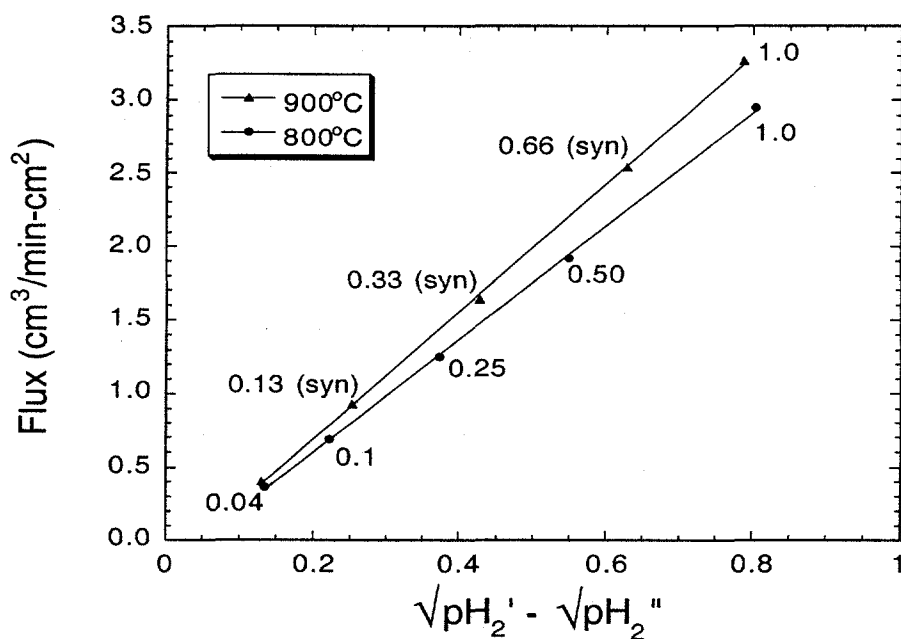


Fig. 3. Dependence of hydrogen flux on partial pressure of hydrogen ( $p_{H_2}$ ) for ANL-3 membrane (0.23-mm-thick). Gas mixtures made from syngas are indicated by "syn."

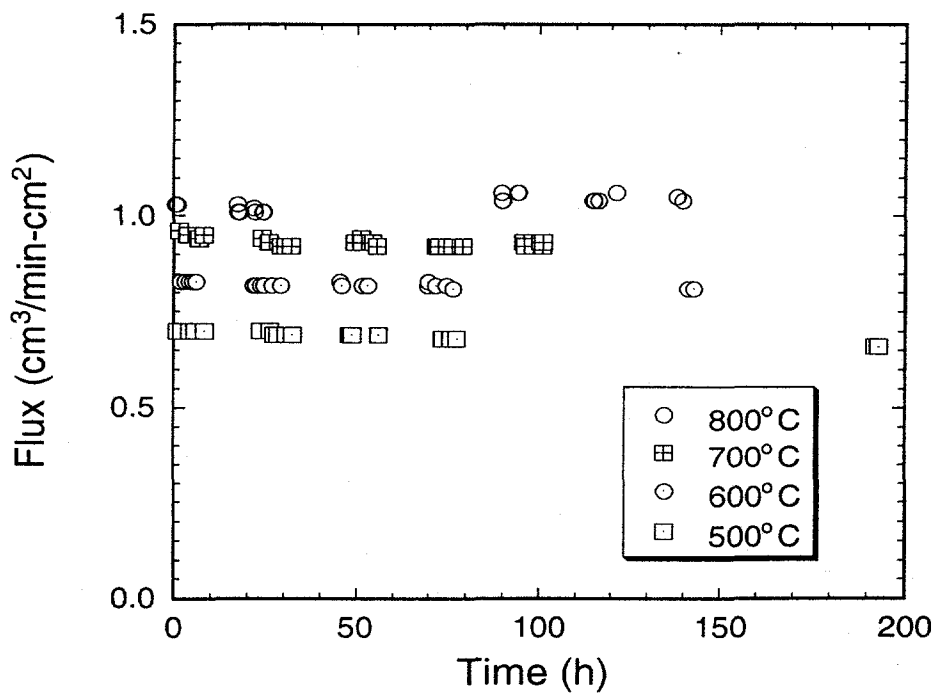


Fig. 4. Hydrogen flux through ANL-3 membrane (0.43-mm-thick) versus time in syngas atmosphere. Feed gas is simulated syngas; sweep gas is 110 ppm  $H_2$ /balance Ar.

#### 4. CONCLUSIONS

We have developed cermet membranes that nongalvanically separate hydrogen from gas mixtures. The highest measured hydrogen flux was  $3.2 \text{ cm}^3(\text{STP})/\text{min}\cdot\text{cm}^2$  for an ANL-3 membrane at  $900^\circ\text{C}$ . For ANL-3 membranes with thicknesses of 0.2-0.5 mm, the permeation rate is limited by the bulk diffusion of hydrogen. The effect of hydrogen partial pressure on the permeation rate confirmed this conclusion and indicates that higher permeation rates can be obtained by decreasing the membrane thickness. Permeation rate in a syngas atmosphere for times of up to 190 h showed no degradation in performance, which suggests that ANL-3 membranes may be suitable for long-term, practical hydrogen separations.

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