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ABSTRACT

Argonne National Laboratory (ANL) and the National Energy Technology Laboratory (NETL) are developing dense ceramic-based membranes for separating hydrogen from the products of coal gasification and other partial-oxidation streams. 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 selectivity is nearly 100% because the membranes contain no interconnected porosity.

Novel cermet (i.e., ceramic-metal composite) membranes have been developed to separate hydrogen from gas mixtures at high temperature and pressure. Hydrogen permeation rates have been measured in the temperature range of 600-900°C for three classes of cermet membranes (ANL-1, -2, and -3). ANL-3a membranes, with a thickness of 40 μm , provide the highest hydrogen flux ($\approx 20 \text{ cm}^3[\text{STP}]/\text{min}\cdot\text{cm}^2$ at 900°C with 100% H_2 as the feed gas). The effects of membrane thickness and hydrogen partial pressure on hydrogen flux indicate that the bulk diffusion of hydrogen is rate-limiting in ANL-3 membranes with a thickness $>40 \mu\text{m}$. ANL-3b membranes were tested in simulated syngas at several temperatures, and no performance degradation was observed for times that approached 200 h; this observation suggests that the membrane is chemically stable and may be suitable for long-term operation. The performance of membranes in separating hydrogen from high-pressure gas streams is being evaluated with NETL's in-house R&D facilities. The present status of membrane development at ANL/NETL will be presented in this paper.

INTRODUCTION

The U.S. Department of Energy's Office of Fossil Energy sponsors numerous programs, the goal of which is to maximize the use of vast domestic fossil resources and ensure a fuel-diverse energy sector while responding to global environmental concerns. Cost-effective, membrane-based reactor and separation processes will help the development of advanced fossil-based power and fuel technologies. Because concerns over global climate change are driving nations to reduce their

CO₂ emissions, hydrogen is considered the fuel of choice for the electric power and transportation industries. Although it is expected that hydrogen will ultimately be generated from renewable sources, technologies based on fossil fuels will supply hydrogen in the interim.

In the present work, dense hydrogen-permeable membranes are being developed 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 the design, fabrication, and operation while minimizing operating costs, membranes will ideally operate in a nongalvanic mode (i.e., operation of the membranes will not involve electrodes or electrical power supply). This ideal requires membrane materials with suitable electronic and protonic conductivities as well as high hydrogen solubility and diffusivity. Good mechanical properties will also be necessary to withstand operating stresses. In addition, the fabricated materials must be thin and dense to maximize the hydrogen flux and maintain high hydrogen selectivity.

Membrane development at Argonne National Laboratory (ANL) and the National Energy Technology Laboratory (NETL) focused initially on BaCe_{0.8}Y_{0.2}O₃ (BCY), because it is a mixed proton/electron conductor with a high total electrical conductivity [1, 2]. However, despite its high total electrical conductivity, the low electronic conductivity of BCY does not allow a high nongalvanic hydrogen flux [3, 4]. To increase the electronic conductivity of BCY-based membranes, and thereby increase their hydrogen flux, various ceramic-metal composite (i.e., cermet) membranes have been developed [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 a metal with high hydrogen permeability is used, it may also provide an additional transport path for the hydrogen.

The cermet membranes are classified as ANL-1, -2, or -3, based on the hydrogen transport properties of the metal and matrix phases. ANL-1 membranes contain a metal with low hydrogen permeability in a matrix of hydrogen-permeable BCY. ANL-2 membranes also have a BCY matrix, but they contain a hydrogen transport metal (i.e., a metal that has a high hydrogen permeability). Although BCY and the metal phase both contribute to the hydrogen flux through ANL-2 membranes, most of the hydrogen diffuses through the metal [7]. In ANL-3 membranes, a hydrogen transport metal is dispersed in a ceramic matrix with low hydrogen permeability, e.g., Al₂O₃ or BaTiO₃. Specific membranes are identified by a number and a letter, where the number represents the type of membrane, e.g., ANL-3 membranes, while the letter indicates a particular combination of metal and matrix phases. For example, ANL-3a is an ANL-3 membrane that contains "metal-a" in a matrix of Al₂O₃, whereas ANL-3b is another ANL-3 membrane that contains a different hydrogen transport metal and/or a different ceramic matrix. In making general comments about an entire class of membranes, a number is used alone without any letter. In this paper, we discuss the state of development of the various cermet membranes (ANL-1, -2, and -3) and compare their hydrogen permeation rates.

EXPERIMENTAL

Cermet membranes contained 40 vol.% metal phase unless otherwise noted. The powders for ANL-1a and -2a membranes were prepared by mixing BCY and metal powders together. The preparation of BCY powder has been described elsewhere [5]. To prepare the powders for ANL-3 membranes, one of two hydrogen transport metals was mixed with ceramic powders that are reported to be poor proton conductors [8]. The powder mixtures were pressed uniaxially to prepare disks (22 mm in diameter x 2 mm thick) for sintering under conditions that were selected on the basis of the membrane composition. ANL-1a and -2a membranes were sintered for 5 h at 1420°C in 4% H₂/balance Ar. ANL-3a membranes were sintered for 5 h at 1400°C in 4% H₂/balance He; ANL-3b membranes, at 1350°C for 12 h in air; and ANL-3d membranes, at 1390°C for 5 h in air.

To measure the permeation rate of a membrane, a sintered disk was polished with 600-grit SiC polishing paper and then affixed to an Al₂O₃ tube with the assembly shown in Fig. 1. With this setup, a seal formed when the assembly was heated to 950°C and spring-loaded rods squeezed a gold ring between the membrane and the Al₂O₃ tube. During sealing, one side of the membrane was purged with 4% H₂/balance He, while the other side was purged with 100 ppm H₂/balance N₂. The typical leakage rate following this procedure is <10% of the total permeation flux.

The flow rate of the sweep gas (100 ppm H₂/balance N₂) during permeation measurements was controlled with an MKS mass flow controller and measured with a Humonics Field-Cal 570 flow calibrator. The sweep gas was analyzed with a Hewlett-Packard 6890 gas chromatograph. Feed

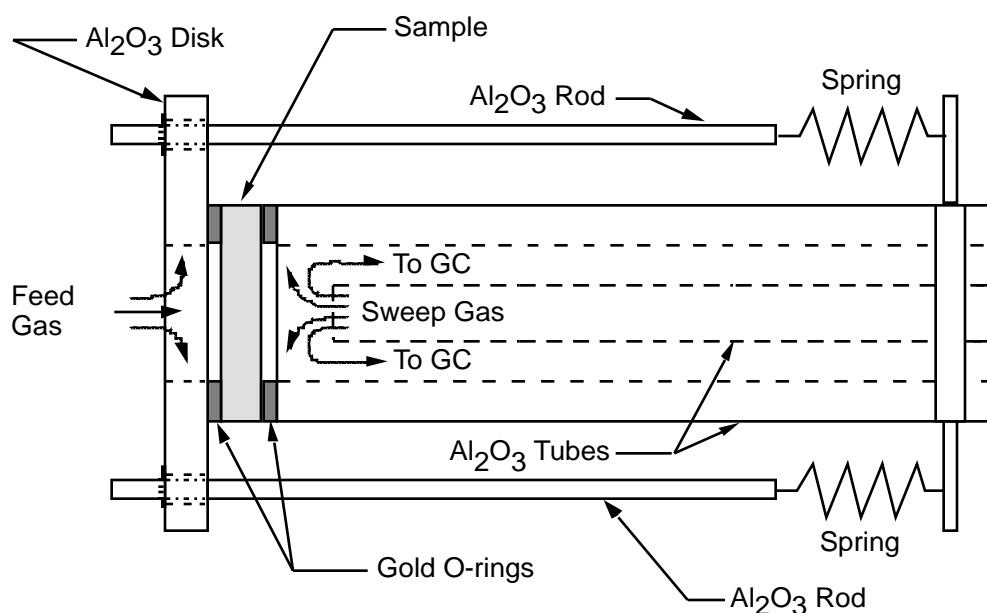


Figure 1. Experimental assembly for measuring hydrogen flux. GC = gas chromatograph.

gases included 100% H₂, simulated syngas (66% H₂, 33% CO, and 1% CO₂), and "dry" or "wet" 4% H₂/balance He. Wet feed gas was obtained by bubbling 4% H₂/balance He through a water bath at room temperature to give 0.03 atm H₂O; dry feed gas was fed directly into the furnace from the gas cylinder. The hydrogen flux through an ANL-3a membrane was measured before and after it was conditioned by heating in air for 250 h at 800°C.

RESULTS

Figure 2 shows the hydrogen permeation rates through ANL-1a, -2a, and -3b membranes when wet 4% H₂/balance He was used as the feed gas. To directly compare permeation properties, the thickness of each membrane was normalized to that of ANL-1a, i.e., 0.50 mm. The actual thickness of each membrane is given in Fig. 2. The permeation rate of ANL-3b was the highest among these membranes, because its metal phase exhibited the highest hydrogen permeability of the various metals tested to date. The permeation rate for ANL-3b was approximately three times higher than that of ANL-1a over the whole temperature range, whereas it was 35% higher than that

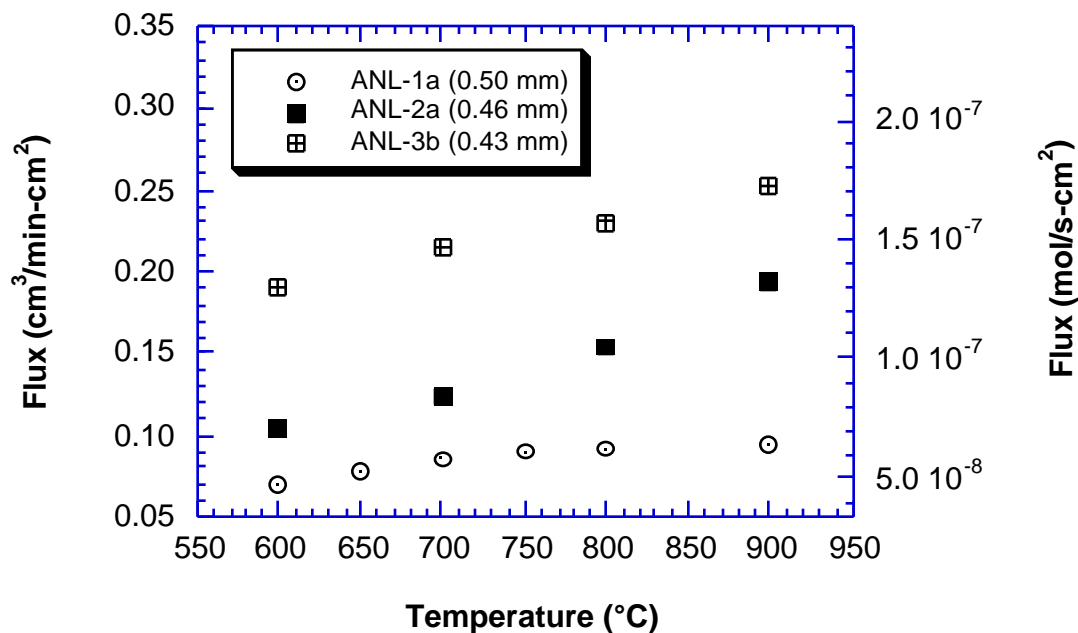


Figure 2. Hydrogen flux for ANL-1a, -2a, and -3b membranes when feed gas was wet 4% H₂/balance He. Thicknesses are normalized to 0.5 mm; true thickness of each membrane is shown in inset.

of ANL-2a at 900°C, and 80% higher at 600°C. The permeation rate of ANL-2a is higher than that of ANL-1a, because ANL-2a contains a hydrogen transport metal whereas ANL-1a does not. The metal in ANL-1a serves only to increase the electronic conductivity of the membrane.

The hydrogen flux through ANL-3b membranes of various thickness is shown in Fig. 3 as a function of temperature when wet 100% H₂ was used as the feed gas. The permeation flux is shown only at 900°C for the 0.1-mm-thick membrane, because the leakage for this membrane increased significantly when the temperature was decreased. With a feed gas of either 100% H₂ (Fig. 3) or 4% H₂/balance He (Fig. 2), the hydrogen flux increased with increasing temperature and was proportional to the inverse of membrane thickness over the whole temperature range. This inverse relationship between flux and thickness indicates that the bulk diffusion of hydrogen is rate-limiting for a thickness >100 μm.

Figure 4 shows the effect of hydrogen partial pressure on the hydrogen flux through ANL-3b (thickness = 230 μm) at 800 and 900°C. At both temperatures, the hydrogen flux varies linearly with the difference in square root of hydrogen partial pressure for the feed and sweep sides of the membrane. This dependence on hydrogen partial pressure is characteristic of bulk-limited hydrogen

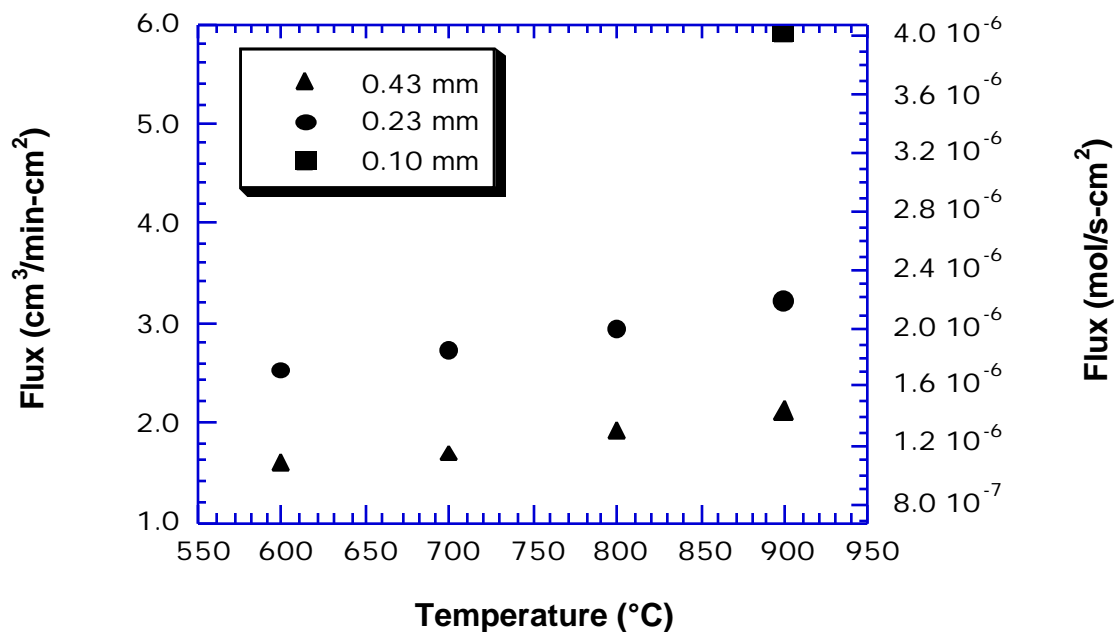


Figure 3. Hydrogen flux through 0.10-, 0.23- and 0.43-mm-thick ANL-3b when the feed gas was wet 100% H₂.

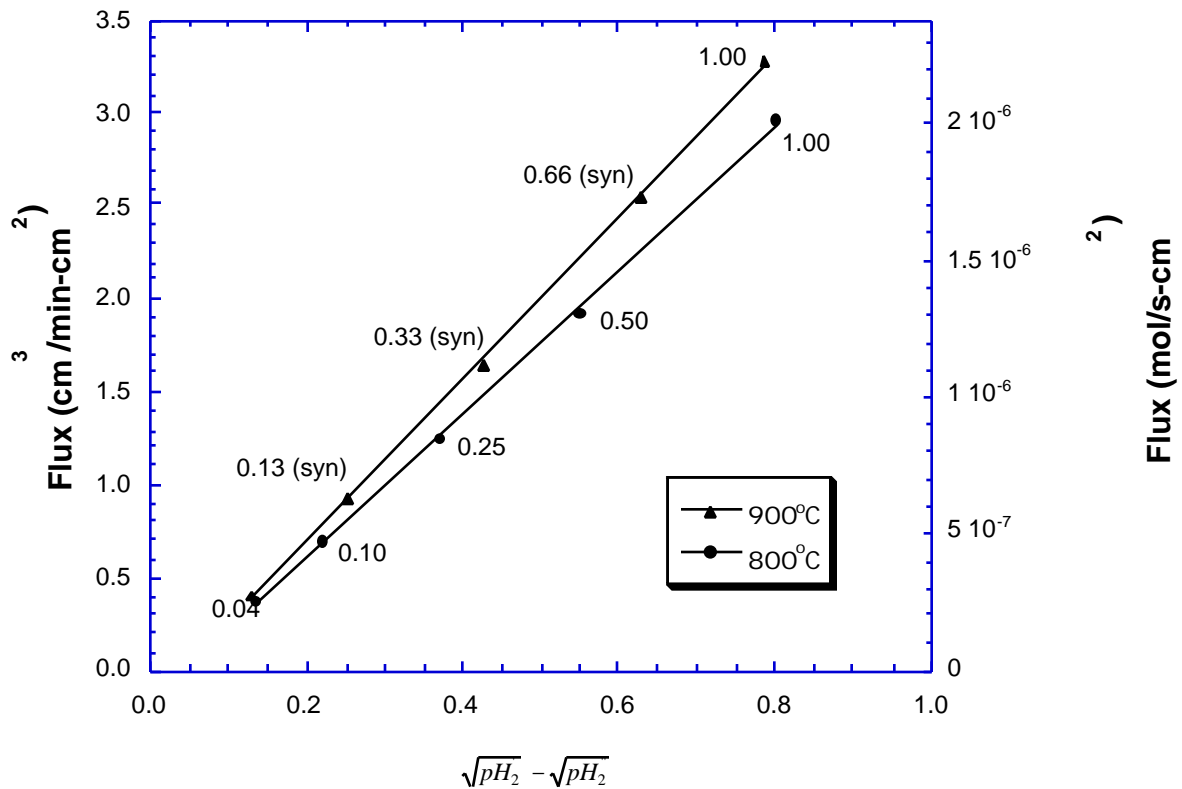


Figure 4. Hydrogen flux through ANL-3b (thickness = 0.23 mm) vs. partial pressure of hydrogen (pH_2). $pH_2' = pH_2$ of feed gas; $pH_2'' = pH_2$ of sweep gas; pH_2 (feed gas) shown on figure; (syn) : gas mixtures made with simulated syngas.

diffusion through metals [9], and confirms that the bulk diffusion of hydrogen through the metal phase dominates the hydrogen flux through ANL-3b membranes in this thickness range. At some lesser thickness, however, interfacial reactions will become rate-limiting.

The chemical stability of ANL-3b in simulated syngas was tested by measuring its hydrogen flux for times up to 190 h in an atmosphere of 66% H_2 , 33% CO , and 1% CO_2 . Figure 5 shows the results for a 0.43-mm-thick membrane. Before and after exposure to syngas at each temperature, feed gas of 4% H_2 /balance He was flowed to determine the leakage rate by measuring the He concentration in the sweep gas. No He leakage was measured at any of the temperatures. The flux showed no noticeable decrease (Fig. 5) during up to 190 h of operation at each temperature. A similar test with another ANL-3b membrane (thickness = 0.23 mm) also showed no decrease in the hydrogen flux during 120 h of exposure to syngas at 900°C.

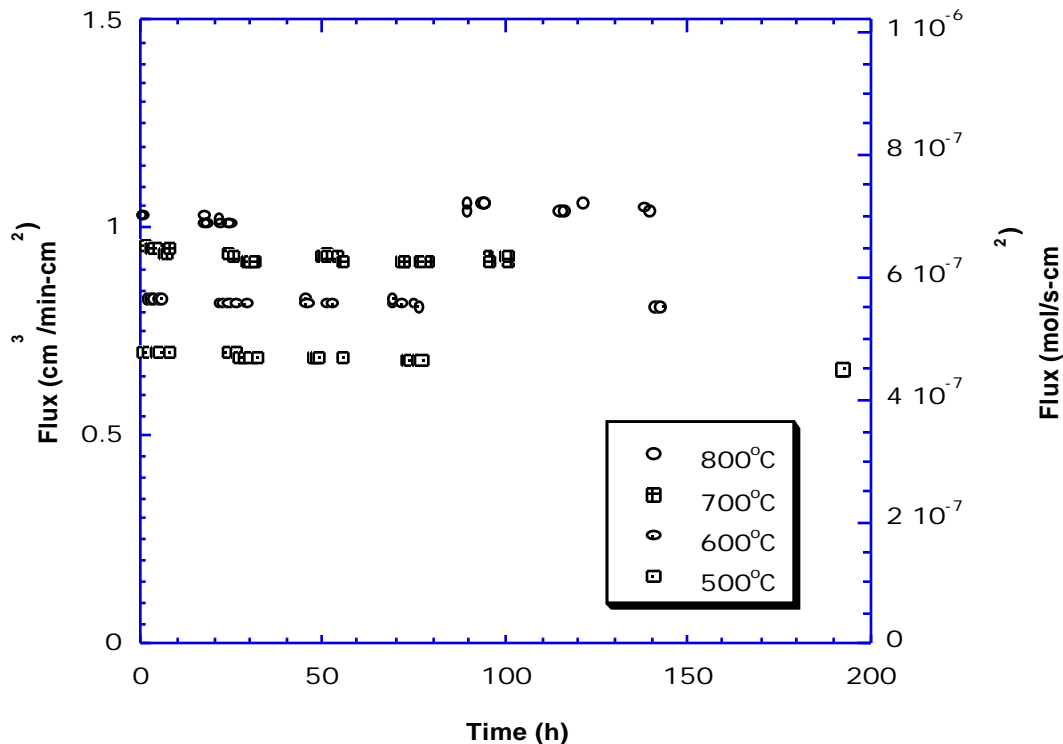


Figure 5. Hydrogen flux through ANL-3b (thickness = 0.43 mm) vs. time in simulated syngas (66% H₂, 33% CO, and 1% CO₂) at various temperatures.

The chemical composition of the ceramic matrix is important for membranes that operate in environments with high concentrations of CO₂. The permeation rates through ANL-2a and -3d are shown in Fig. 6 as a function of time at 900°C in dry and wet syngas of composition 2.0% CH₄, 19.6% H₂, 19.6% CO, and 58.8% CO₂ (mol.%). The Al₂O₃ matrix of ANL-3d is clearly more stable than the BCY matrix of ANL-2a. The hydrogen flux through ANL-2a decreased dramatically after only several minutes, whereas the flux through ANL-3d was stable for >3 h. Examination of the ANL-2a surface by scanning electron microscopy after permeation measurements showed that the BCY matrix had decomposed to form BaCO₃ and other phases. A chemically stable matrix such as Al₂O₃ or ZrO₂ is obviously required for the membrane to operate in atmospheres that contain high concentrations of CO₂.

Of the various ANL membranes, ANL-3a has exhibited the highest hydrogen flux to date. In Fig. 7, the hydrogen flux through ANL-3a (50 vol.% metal, thickness = 40 μm) is shown as a function of temperature before and after it was conditioned in air. Before conditioning, the hydrogen flux of the membrane was 16.2 cm³(STP)/min-cm² at 900°C with 100% H₂ as the feed gas; however, its flux at 400°C (0.8 cm³(STP)/min-cm²) was much lower than predicted

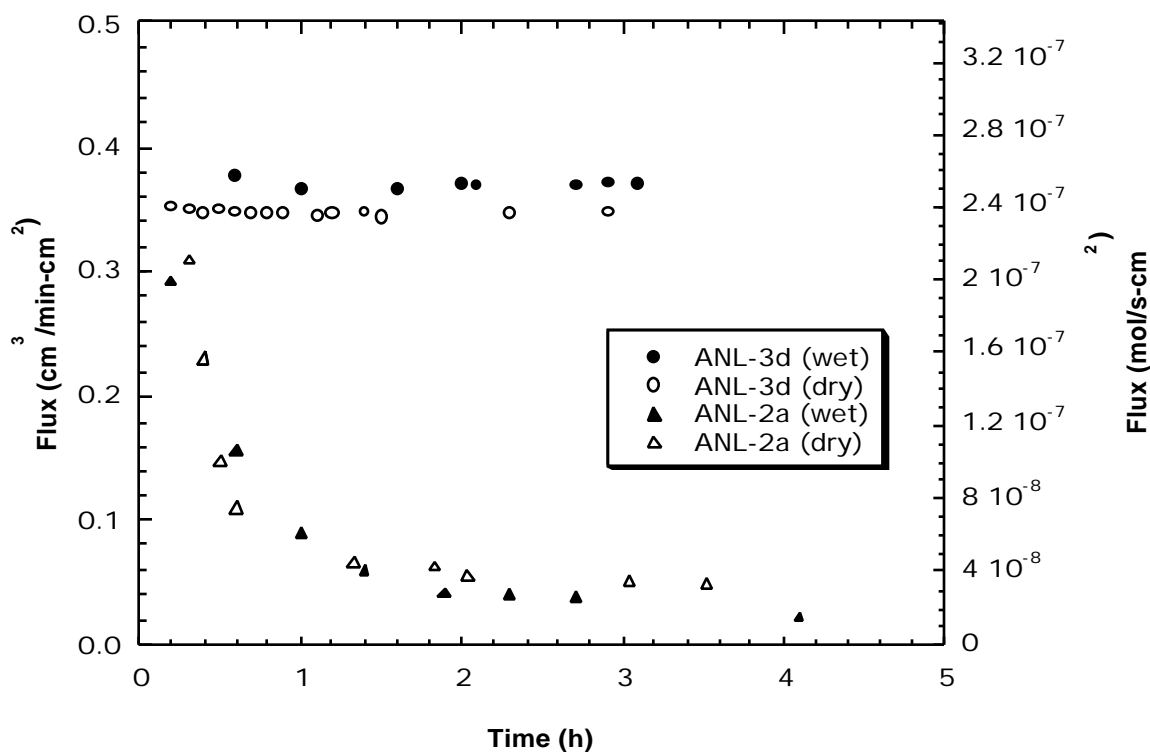


Figure 6. Hydrogen flux through Al_2O_3 -based ANL-3d (thickness = 0.53 mm) and BCY-based ANL-2a (thickness = 0.43 mm) in a feed gas containing 2.0% CH_4 , 19.6% H_2 , 19.6% CO , and 58.8% CO_2 (mol.%).

from known hydrogen permeabilities of the membrane materials. After the membrane was conditioned by heating in air for 250 h at 800°C, its hydrogen flux increased to 20.0 at 900°C and 7.6 $\text{cm}^3(\text{STP})/\text{min-cm}^2$ at 400°C. Conditioning produced only a marginal increase in the flux at 600°C. The effect of conditioning on the hydrogen flux is not understood at present.

The significantly higher hydrogen flux through ANL-3a can be attributed to two main factors. First, its concentration of hydrogen transport metal (50 vol.%) is higher than that of other membranes, and second, it is considerably thinner than the other membranes (40 μm vs. 100 μm for the thinnest ANL-3b membrane, shown in Fig. 3). While both factors produce a higher flux through ANL-3a, most of its higher flux can be explained by its reduced thickness, indicating that the bulk diffusion of hydrogen is rate-limiting to a thickness of 40 μm , and suggesting that thinner (<40 μm) membranes may yield an even higher flux.

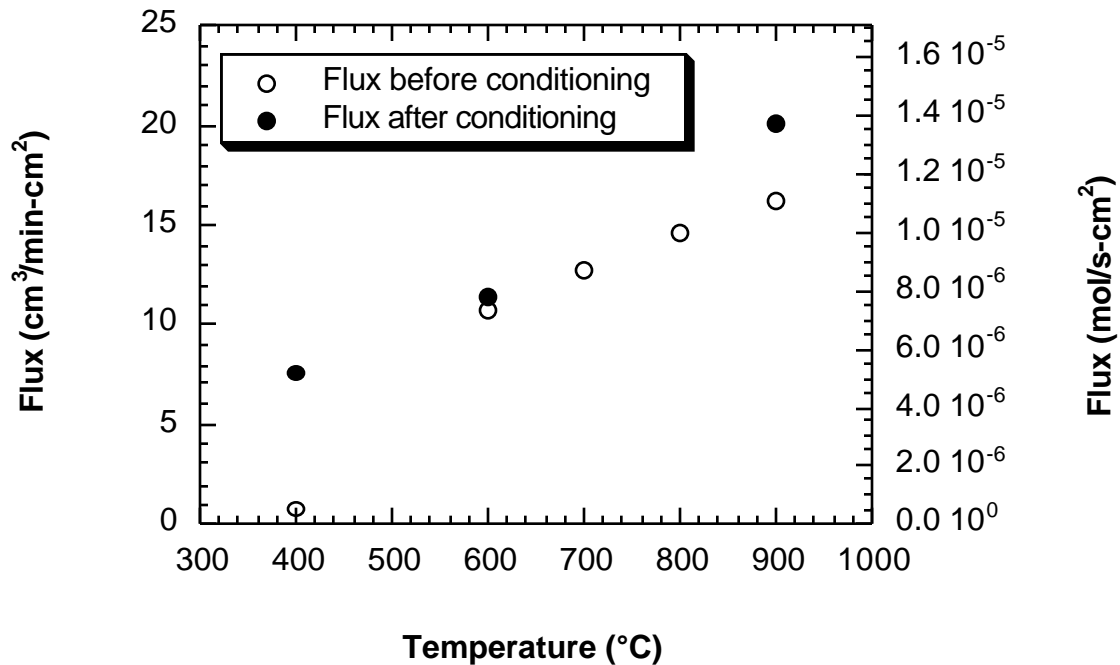


Figure 7. Hydrogen flux through ANL-3a membrane (thickness = 0.04 mm) before and after conditioning for ≈ 250 h at 800°C in air. Feed gas for flux measurements was 100% H_2 . Membrane contained 50 vol.% of a hydrogen transport metal.

CONCLUSIONS

Cermet membranes developed at ANL can separate hydrogen from gas mixtures without the use of electrodes or an electrical power supply. A hydrogen flux of $20.0 \text{ cm}^3(\text{STP})/\text{min-cm}^2$ was measured at 900°C for an ANL-3a membrane that had been conditioned by heating in air at 800°C . The dependence of hydrogen flux on hydrogen partial pressure indicates that the bulk diffusion of hydrogen through the metal phase limits hydrogen permeation through ANL-3 membranes with thickness of 40-500 μm . This finding suggests that higher permeation rates may be obtained by decreasing the membrane thickness. The hydrogen flux through ANL-3b in simulated syngas showed no degradation in performance for times up to 190 h, indicating that the membranes may be suitable for long-term, practical hydrogen separation.

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