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# High Temperature Protonic Conductors

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# Mixed-Conducting Membranes for Hydrogen Production and Separation

U. (Balu) Balachandran, Beihai Ma, Tae H. Lee, Sun-Ju Song, Ling Chen, and Stephen E. Dorris
Energy Systems Division, Argonne National Laboratory, Argonne, IL, 60439

## ABSTRACT

Mixed-conducting oxides, possessing both ionic and electronic charge carriers, have found wide application in recent years in solid-state electrochemical devices that operate at high temperatures, e.g., solid-oxide fuel cells, batteries, and sensors. These materials also hold promise as dense ceramic membranes that separate gases such as oxygen and hydrogen from mixed-gas streams. We are developing Sr-Fe-Co oxide (SFC) as a membrane that selectively transports oxygen during partial oxidation of methane to syngas (mixture of CO and $H_2$) because of SFC's high combined electronic and ionic conductivities. We have evaluated extruded tubes of SFC for conversion of methane to syngas in a reactor that was operated at ≈900°C[AEI]. Methane conversion efficiencies were >90%, and some of the reactor tubes were operated for >1000 h. We are also developing dense proton-conducting oxides to separate pure hydrogen from product streams that are generated during methane reforming and coal gasification. Hydrogen selectivity in these membranes is nearly 100%, because they are free of interconnected porosity. Although most studies of hydrogen separation membranes have focused on proton-conducting oxides by themselves, we have developed cermet (i.e., ceramic-metal composite) membranes in which metal powder is mixed with these oxides in order to increase their hydrogen permeability. Using several feed gas mixtures, we measured the nongalvanic hydrogen permeation rate, or flux, for the cermet membranes in the temperature range of 500-900°C. This rate varied linearly with the inverse of membrane thickness. The highest rate, ≈32 $cm^3$(STP)/min-$cm^2$, was measured at 900°C for an ≈15-μm-thick membrane on a porous support structure when 100% $H_2$ at ambient pressure was used as the feed gas.

## INTRODUCTION

Hydrogen is expected to play a vital role in the transportation sector via fuel cell vehicles (FCVs) and in the distributed power generation market via stationary fuel cells because of concerns over global climate change. One of the crucial requirements for successfully introducing FCVs is a low-cost supply of hydrogen. At present, petroleum refining and the production of ammonia and methanol collectively consume ≈95% of all manufactured hydrogen in the U.S. Most of the demands for hydrogen are currently met by steam reforming of methane and naphtha reforming (mainly in refineries). In the first stage of steam reforming, methane is oxidized to form syngas (a mixture of hydrogen and carbon monoxide). The syngas is then subjected to a water-gas shift reaction, which converts carbon monoxide to additional hydrogen and carbon dioxide, and hydrogen is separated from this stream. Steam reforming is usually very energy- and capital-intensive, requiring high temperatures and pressures. Although direct partial oxidation of methane with air as the oxygen source is a potential alternative to the steam reforming process, downstream processing requirements cannot tolerate nitrogen, and therefore, pure oxygen is required. Thus, the most significant cost associated with partial oxidation is that of the oxygen plant.

Mixed-conducting oxides, with both ionic and electronic charge carriers, have found wide application in recent years in high-temperature solid-state electrochemical devices such as solid-oxide fuel cells, batteries, and sensors. These materials also hold promise as dense ceramic membranes for separating gases such as oxygen and hydrogen from mixed-gas streams. Dense ceramic membranes offer potential solutions to several problems in methane-to-hydrogen conversion. Because mixed-conductors transport both ions (oxygen or hydrogen) and electrons, no external electrodes are required for gas separation. Such a system will operate nongalvanically (i.e., without an externally applied electrical potential). The chemical potential gradient across the membrane is the driving force for the gas separation. The classical material used in solid-state transport of oxygen is zirconia stabilized either by calcia or yttria. This material transports oxygen ions from the oxygen-rich side to the oxygen-deficient side of the membrane, but electrodes are required to transfer the electrons, because stabilized zirconia is an effective electronic insulator. The extremely low electronic conductivity of zirconia requires the use of electrodes and an external short circuit and thereby makes this material unsuitable for large-scale commercial separation of oxygen. [AE2]

A successful approach has been to use materials that contain both ionic and electronic conductivity, e.g., $ABO_3$-type perovskites doped on the A and/or B sites [1-4]. The perovskite $SrFe_{0.2}Co_{0.8}O_{3-\delta}$ has good electronic and ionic conductivities at 800°C in air [5]. However, this material lacks structural stability when it is exposed to large gradients in the oxygen partial pressure ($pO_2$) [6]. This instability makes it unsuitable as a dense ceramic membrane for the partial oxidation of methane to syngas. A non-perovskite mixed-conducting oxide, $SrFeCo_{0.5}O_{3\pm\delta}$ (SFC), was found to have not only higher oxygen permeability but also structural stability in both oxidizing and reducing environments [7,8]. With these properties, SFC makes an excellent oxygen transport membrane (OTM).

We are also developing dense, hydrogen-permeable membranes for separating hydrogen from mixed gases at commercially significant fluxes. Of particular interest is the separation of hydrogen from product streams that are generated during methane partial oxidation, water-gas shift reactions, and coal gasification. Because the membrane will nongalvanically separate pure hydrogen, it requires materials that exhibit suitable electronic and protonic conductivities as well as high hydrogen diffusivity and solubility. Initially, we focused our efforts on $BaCe_{0.8}Y_{0.2}O_{3-\delta}$ (BCY), a mixed proton/electron conductor whose high total electrical conductivity [9,10] suggested that it might yield a high hydrogen flux. Early results showed, however, that the electronic conductivity of BCY is insufficient to support a high nongalvanic hydrogen flux [11,12]. To increase the electronic conductivity and thereby increase the hydrogen flux, we have developed various cermet (i.e., ceramic-metal composite) membranes in which suitable metal powder is dispersed in a ceramic matrix [13]. In these cermets, the metal enhances the hydrogen permeability of the ceramic phase by increasing the electronic conductivity of the composite. If the metal has high hydrogen permeability, it is called a hydrogen transport metal and can provide an additional transport path for hydrogen. A cermet membrane containing 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 [$\approx 32$ $cm^3$(STP)/min-$cm^2$] and functions well as a hydrogen transport membrane (HTM).

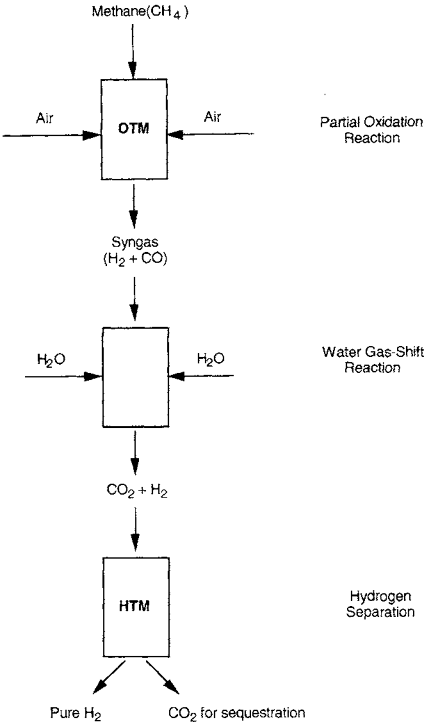

Fig. 1. Flow diagram showing process for using dense ceramic membranes (OTM and HTM) to convert methane to high-purity hydrogen.

Figure 1 [AE3]illustrates a process by which pure hydrogen can be efficiently produced from methane using both the OTM and HTM. In the first step of the process, an OTM selectively removes oxygen from air, allowing it to diffuse through the dense membrane, where it reacts, in the presence of a reforming catalyst, with methane to form syngas. When steam is injected into the syngas in the presence of a catalyst, the carbon monoxide converts to additional hydrogen and carbon dioxide through the water gas-shift reaction. An HTM then separates this product gas into streams of pure hydrogen and carbon dioxide.

In this paper, we report our test results on the oxygen-permeable SFC membranes and hydrogen-permeable cermet membranes. Oxygen permeation is measured as a function of temperature in a gas-tight electrochemical cell. Extruded hollow tubes of SFC are evaluated in a reactor operating at ≈850°C for conversion of methane into syngas. The permeation rate of hydrogen through dense cermet membranes is presented as a function of membrane thickness and temperature.

## EXPERIMENTAL

Oxygen-permeable SFC samples were prepared by solid-state reaction among appropriate amounts of $SrCO_3$, $Fe_2O_3$, and $Co(NO_3)_2{\cdot}6H_2O$. Mixing and grinding were performed in isopropanol using a zirconia milling medium. After drying, the mixtures were calcined at ≈850°C for ≈16 h with intermittent grinding. The resultant powders were pressed into pellets and sintered at ≈1200°C for ≈5 h. Sintered pellets were polished and used for oxygen permeation tests. A gas-tight electrochemical cell was used in the oxygen permeation experiments. The experimental set-up used to study oxygen permeation of SFC membranes was reported earlier [14]. Hollow tube membranes (outer diameter, ≈6.5 mm; wall thicknesses, ≈0.25-1.2 mm; length, <30 cm) were fabricated by plastic extrusion. The tubular membranes were evaluated for performance in a reactor system described earlier [6, 16[AE4]]. A Rh-based reforming catalyst was loaded adjacent to the tube, and a gold wire mesh was wrapped around the SFC tube to prevent a reaction between the catalyst and the ceramic tube. Both the feed gas (80% methane, 20% argon) and the effluents were analyzed by gas chromatography.

The powder mixture used for fabricating self-supported cermet HTM was prepared by mechanically mixing ≈40-60 vol.% of a hydrogen transport metal with a ceramic powder that can be sintered relatively easily. The powder mixture was pressed into disks and sintered at ≈1400°C for ≈5 h. For the hydrogen permeation tests, both sides of the disks were polished to obtain the desired thickness and produce faces that were flat and parallel to one another. Thin-film cermet membranes were made by painting a viscous slurry of the HTM components onto a porous, partially sintered $Al_2O_3$ substrate, and then sintering for 5 h at 1400°C in air. To prepare the slurry, the ceramic and metal HTM components were dispersed in a solution of α-terpineol and isopropyl alcohol with polyvinyl butyral as a binder and dibutyl phthalate as a plasticizer. The porous substrate was prepared by uniaxially pressing $Al_2O_3$ powder into a disk and pre-sintering for 3 h at 700-800°C in air. Thin film membranes were not polished before their permeation rates were measured. The hydrogen permeation rate (i.e., hydrogen flux) was measured by a procedure described elsewhere [17].

## RESULTS AND DISCUSSION

The oxygen flux of SFC was determined with a gas-tight cell in the temperature range 600-900°C. Reducing environments were achieved by removing oxygen from the gas-tight cell by means of pumping electrodes attached to the yttria-stabilized zirconia crucible [15]. Oxygen permeates through the SFC disk membrane because of the oxygen partial pressure difference between the two sides of the specimen disk. At 900°C, an oxygen flux of ≈2.5 $cm^3$ (STP)/min-$cm^2$ was measured for a ≈2.9-mm-thick disk specimen when one side of the SFC disk was exposed to air and the other side to a $pO_2$ of $\approx 10^{-10}$ atm. Oxygen flux values that were measured in gas-tight cell experiments are plotted in Fig. 2 as a function of temperature. The oxygen flux increases with increasing temperature and decreasing membrane thickness.

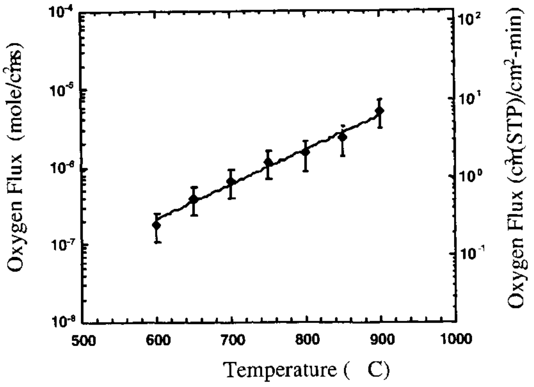

Fig. 2[AE5]. Temperature-dependent oxygen permeation flux in SFC membrane.

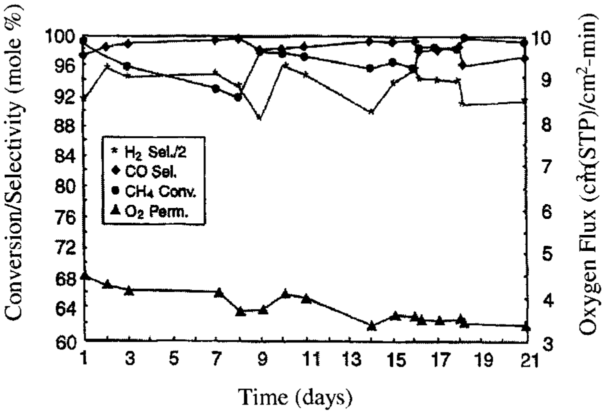

Fig. 3. Methane conversion, CO and $H_2$ selectivities, and oxygen permeation flux in an SFC membrane reactor operated with reforming catalyst for 21 days at 900°C (80% $CH_4$/20% Ar feed, pressure ≈1 atm).

The performance of extruded SFC tubes was evaluated in a quartz methane conversion reactor that was described earlier [6]. Data obtained with the reactor using an SFC membrane tube are plotted in Fig. 3. The fuel (80% methane, 20% argon) was fed at ≈1 atm pressure along the shell side of the SFC tube. Air at ambient pressure was passed through the inside of the tube. Oxygen from air was selectively transported through the membrane, where it reacted with methane in the presence of the reforming catalyst to produce syngas. High methane conversion efficiency (≈98%) and high CO selectivity (>96%) were observed. The reactor was deliberately shut down after 21 days. To further confirm the stability of the SFC membrane, we operated another reactor with a different feed gas over a period of 1000 h, as shown in Fig. 4. This time the reactor was supplied with a mixture that is typically expected in a commercial recycle feed, namely, ≈17% methane, ≈20% carbon monoxide, ≈9% carbon dioxide, ≈44% hydrogen, and ≈10% argon. Again, high methane conversion efficiency was observed. However, the oxygen flux during this operation slowly decreased from ≈4 to ≈2 $cm^3$(STP)/min-$cm^2$. To use the SFC membrane tube in converting methane to syngas, it appears critical to reduce the wall thickness [AE6]of the tube. Reducing the wall thickness increases the oxygen flux across the membrane and maximizes the surface-area-to-volume ratio, which allows the reactor size to be reduced.

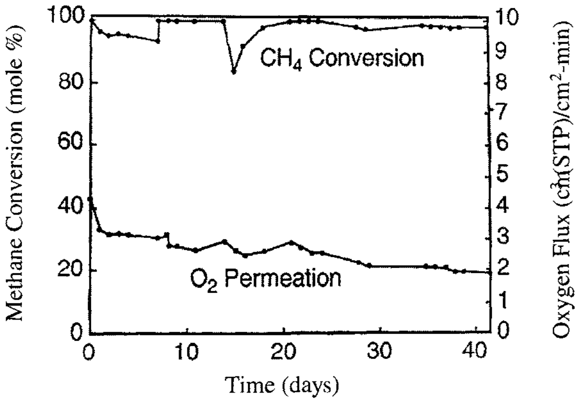

Fig. 4. Methane conversion efficiency and oxygen flux for reactor using SFC ceramic tube with mixed gas feed (17% $CH_4$, 20% CO, 9% $CO_2$, 44% $H_2$ and 10% Ar). Conditions: temperature, 900°C; pressure, 1 atm; and flow rate, 20 $cm^3 \cdot min^{-1}$.

Hydrogen flux through cermet HTMs of different thicknesses was measured at various temperatures. Figure 5 shows the temperature dependence of hydrogen flux through an HTM with thickness of ≈22 μm. The feed gas was 100% hydrogen, and the sweep side was nitrogen with ≈100 ppm hydrogen. Both the feed and the sweep gases were at ambient pressure. The hydrogen flux was measured in the temperature range 600-900°C. A hydrogen flux of ≈20 $cm^3$(STP)/min-$cm^2$ was observed at 900°C. The chemical stability of the cermet membrane in simulated syngas (66% hydrogen, 33% carbon monoxide, and 1% carbon dioxide) was tested by measuring its hydrogen flux at several temperatures for times up to ≈200 h. No noticeable decrease in flux was observed during up to ≈200 h of operation at each temperature (500-800°C).

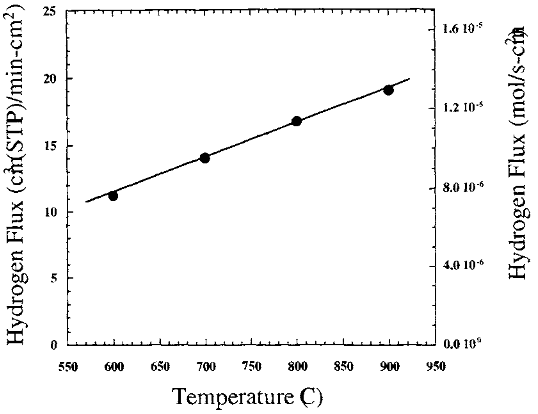

Fig. 5. Hydrogen flux through ≈22-µm-thick self-supported cermet membrane versus temperature using 100% $H_2$ as the feed gas.

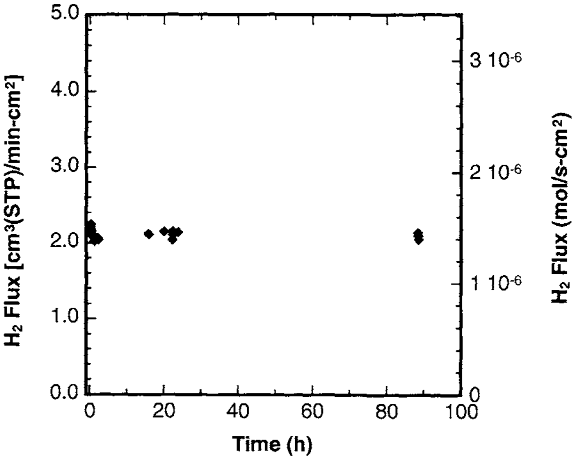

Fig. 6. Hydrogen flux for ≈200-µm-thick cermet membrane at 900°C in $H_2S$-containing simulated syngas: 61.3% $H_2$, 8.2% $CH_4$, 11.5% CO, 9.0% $CO_2$, 10% He, 100 ppm $H_2S$.

The chemical stability of a 200-µm-thick cermet membrane was tested in simulated synthesis gas (61.3% $H_2$, 8.2% $CH_4$, 11.5% CO, 9.0% $CO_2$, and 10% He) at 900°C by measuring its hydrogen flux versus time. To measure the leakage of the feed gas through the seal, we analyzed the concentration of He in the sweep gas. After the membrane had been exposed to this gas for

≈4 h, $H_2S$[AE7] (100 ppm) was added to the feed gas. Figure 6 shows that the flux decreased ≈10% in the first hour, and then stabilized or increased slightly during ≈90 h of exposure to the synthesis gas with $H_2S$. The reason for the initial decrease in flux is not understood at this time.

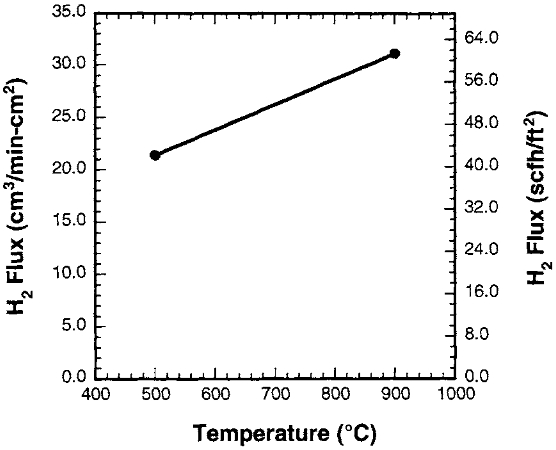

Fig. 7. Hydrogen flux through ≈15-µm-thick cermet membrane on a porous substrate at 500 and 900°C using 100% $H_2$ at ambient pressure as the feed gas.

Figure 7 shows the hydrogen flux for a ≈15-µm-thick cermet membrane on a porous substrate at 500 and 900°C. This membrane gave record high flux values (for Argonne membranes) of ≈22 $cm^3$(STP)/min-$cm^2$ at 500°C and ≈32 $cm^3$(STP)/min-$cm^2$ at 900°C. The feed gas was 100% $H_2$. Both the feed and the sweep gases were at ambient pressure. Figure 8 shows the effect of hydrogen partial pressure on the flux through the ≈15-µm-thick cermet membrane on a porous substrate at 500 and 900°C. At both temperatures, the hydrogen flux increases linearly with the difference in the square root of hydrogen partial pressure in the feed and sweep gases. This behavior is characteristic of bulk-limited hydrogen diffusion through a metal [18] and is expected because the membrane contains a hydrogen transport metal and the ceramic phase has low hydrogen permeability. Extrapolating the experimentally measured values at atmospheric pressure to high-pressure (≈300 psig) feed streams (dotted lines in Fig. 8) yields flux values over 200 $cm^3$/min-$cm^2$ at 900°C and over 100 $cm^3$/min-$cm^2$ at 500°C.