II.B.6 Hydrogen Production by NG and Renewable Liquids Reforming using Dense Ceramic Membranes

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Objectives

- Measure H_2 production rate using oxygen transport membranes (OTMs).
- Optimize OTM performance by doping and controlling OTM's microstructure.
- Fabricate thinner OTMs to enhance their H_2 production rate.

Technical Barriers

This project addresses the following technical barriers from the Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Reformer Capital Costs
(B) Reformer Manufacturing
(C) Operation and Maintenance (O&M)
(N) Hydrogen Selectivity
(R) Cost

Technical Targets

This project is developing compact dense ceramic membranes that transport pure oxygen to efficiently and cost-effectively produce hydrogen by reforming natural gas (NG) and renewable liquid fuels such as ethanol and bio-oil. Cost-effective small-scale reformer technology will be developed to integrate process steps, thereby minimizing unit size, capital cost, energy use, and operating cost and helping to meet DOE targets:

- Production Unit Efficiency:
  - 75.0% lower heating value (LHV) by 2015 for NG
  - 72.0% (LHV) by 2012 for bio-derived liquids
- Production Unit Capital Cost (un-installed): $580K by 2015 for NG
  - $1.0M by 2012 for bio-derived liquids
- Total Hydrogen Cost:
  - $2.00/gge by 2015 for NG
  - $3.80/gge by 2012 for bio-derived liquids
 - <$3.00/gge by 2017 for bio-derived liquids

Accomplishments

- Hydrogen production rates were measured using two types of OTM: $SrFeCo_{0.5}O_x$ (SFC2) and SFT (Sr-Fe-Ti oxide).
- Confirmed that decreasing OTM thickness increases hydrogen production rate if OTM surfaces are modified to overcome limitations from surface reaction kinetics.
- Thin (0.25-0.50 mm) SFC2 membranes were coated with porous SFC2 layers to obtain the highest hydrogen production rate yet obtained at Argonne, 11 cm^3/min-cm^2.
- SFC2 thin (<0.10 mm) films were fabricated on porous substrates.

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Introduction

The dissociation of water, shown by reaction (1), generates very low concentrations of hydrogen and oxygen even at relatively high temperatures (e.g., 0.1% hydrogen and 0.042% oxygen at 1600°C), because the equilibrium constant for dissociation is small.

$$H_2O(g) \Leftrightarrow H_2 + \frac{1}{2}O_2 \qquad (1)$$
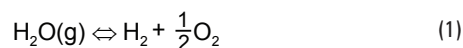
However, significant amounts of hydrogen and oxygen can be generated at moderate temperatures if a mixed-conducting (i.e., electron- and ion-conducting) membrane is used to separate oxygen and hydrogen. For example, if an OTM is used to remove oxygen from the water-splitting zone, the steam becomes richer in hydrogen while oxygen is transported to the other side of the membrane, where it can be used to reform NG and/or renewable liquid fuels. Because the OTM is a

mixed conductor, the oxygen transport requires neither electrodes nor external power circuitry, i.e., the process is nongalvanic. The hydrogen production rate depends directly on the rate at which oxygen is removed from the water dissociation zone, which depends on the oxygen permeation rate through the membrane. The oxygen permeation rate is a function of the membrane's electron and oxygen-ion conductivities, its surface oxygen exchange kinetics, and the oxygen partial pressure (pO_2) gradient across the membrane.

We measured significant hydrogen production rates using an OTM composed of an oxygen ion conductor (Gd-doped CeO_2 [CGO]) and an electronic conductor (Ni). The hydrogen production rate increased with increases in temperature, water partial pressure on the hydrogen-production side of the membrane, and oxygen chemical potential gradient across the membrane. It also increased as the OTM thickness decreased, but surface reaction kinetics began to limit hydrogen production for thin (<0.5 mm) OTMs. To enhance the surface reaction kinetics of thin OTMs, we increased their active area by coating them with porous layers, and we made their microstructures finer to increase their triple-phase-boundary area, i.e., the region where ionic conductor, electronic conductor, and gas phase meet. Without any microstructural modifications, high hydrogen production rates were achieved using thick (>0.5 mm) OTMs made of SFC2, developed by our group to separate oxygen from air. To increase SFC2's hydrogen production rate, we developed techniques for fabricating thin films with microstructural modifications that enhance surface reaction kinetics. To increase hydrogen production during methane reforming, steam was added to methane in the presence of a steam-reforming catalyst. We began developing and utilizing a model to assess the economic potential of using an OTM to produce hydrogen during the reforming of NG and bio-derived liquids.

Approach

A system analysis will be done to determine the requirements for a reactor that would use an OTM to cost-effectively produce hydrogen during the reforming of NG and renewable liquids. For cost-effective hydrogen production, the OTM must efficiently transport the oxygen needed for reforming. To do so, the OTM needs an appropriate combination of electronic and ionic conductivity, which we will assess by measuring the conductivity of promising membrane materials. We will measure the hydrogen production rate of materials that have sufficient conductivity ($>10^{-1}$ ohm^{-1}-cm^{-1}), and will drive the removal of oxygen by using a reactive gas to establish an oxygen partial pressure (pO_2) gradient across the membrane. In order to increase the oxygen flux, and hence the hydrogen production rate, we will decrease the membrane thickness and modify selected membranes in two ways. Catalysts will be used to

promote reactions, and/or the microstructure will be manipulated to enhance reaction kinetics at the surface of the membrane. If steam is used as the source of oxygen, the water-splitting equilibrium shifts away from dissociation as the steam becomes enriched in hydrogen; therefore, less water dissociates, and overall hydrogen production is less efficient than it could be. To overcome this limitation, we will remove hydrogen from the steam using a hydrogen transport membrane (HTM) in parallel with the OTM. In order for OTMs to cost-effectively produce hydrogen, they must have good chemical and mechanical stability; therefore, we will evaluate the stability of OTMs during hydrogen-production by reforming of NG and renewable liquid fuels.

Results

Both flat surfaces of thin (0.25-0.50 mm) SFC2 membranes were coated with porous SFC2 layers to increase the membranes' hydrogen production rate. Figure 1 compares the hydrogen production rates of surface-modified and unmodified SFC2 membranes, measured at 900°C using wet N_2 (pH_2O=0.49 atm) on the membranes' hydrogen-generation side and dry H_2 (pH_2=0.8 atm) on the oxygen permeate side. Porous SFC2 layers increased the surface area of coated membranes and significantly increased their hydrogen production rate relative to unmodified membranes. A 0.25-mm-thick membrane had a rate of 11 cm^3/min-cm^2, the highest hydrogen production rate yet obtained at Argonne. The effect of porous layers becomes more pronounced as the membrane thickness decreases, because surface oxygen exchange kinetics become more dominant. Ni/CGO cermet membranes showed a similar effect in previous studies. Although the porous
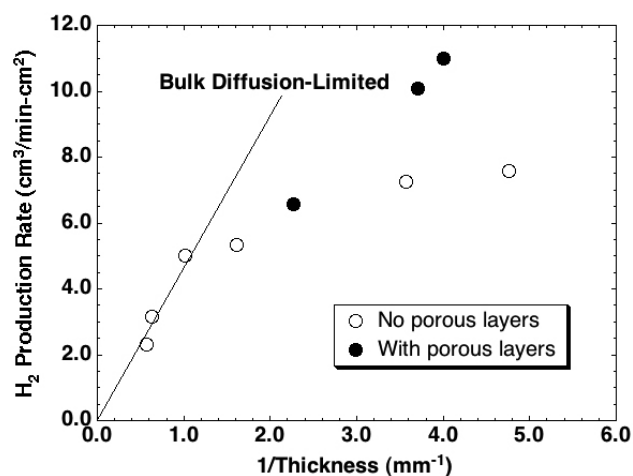

FIGURE 1. H_2 production rate at 900°C vs. inverse of thickness for SFC2 membranes with and without porous SFC2 layers, measured with wet N_2 (pH_2O=0.49 atm) on the hydrogen-generation side and dry H_2 (pH_2=0.8 atm) on the oxygen permeate side. Line indicating bulk diffusion-limited regime is drawn only to aid the eye.

layers clearly enhanced the hydrogen production rate, they did not eliminate limitations from surface reaction kinetics, as shown by the fact that the data for membranes with porous layers do not fall on the extrapolation for samples limited by bulk diffusion. Modifying the microstructure of the porous layers might further enhance the surface reaction kinetics and hydrogen production rate.

Figure 1 indicates that decreasing the membrane thickness can further increase the hydrogen production rate if limitations from surface reaction kinetics are overcome by coating the membranes with porous layers. To prepare thin membranes with sufficient mechanical integrity for routine handling, we are developing methods to fabricate SFC2 films on porous substrates. SFC2 thin ($\approx$40-μm) films have been prepared on substrates consisting of porous Ni/CGO or porous SFC2. An SFC2 film on porous Ni/CGO gave a hydrogen production rate that was much lower than expected, possibly due to reaction between SFC2 and Ni. In addition, a bond layer for improving adhesion between the SFC2 film and Ni/CGO substrate contains a low volume fraction ($\approx$50%) of SFC2, which might restrict oxygen permeation. To avoid these problems with Ni/CGO substrates, SFC2 thin films were fabricated on porous SFC2 substrates. The hydrogen production rate of such a film has not been measured yet, but a cross-sectional view (Figure 2) suggests that the film is dense, the substrate has sufficient porosity, and there appears to be good bonding between the film and substrate.

SFC2 is a promising material for OTMs due to its high hydrogen production rate at high temperatures (>850°C); however, a phase transition at 825-850°C dramatically reduces its hydrogen production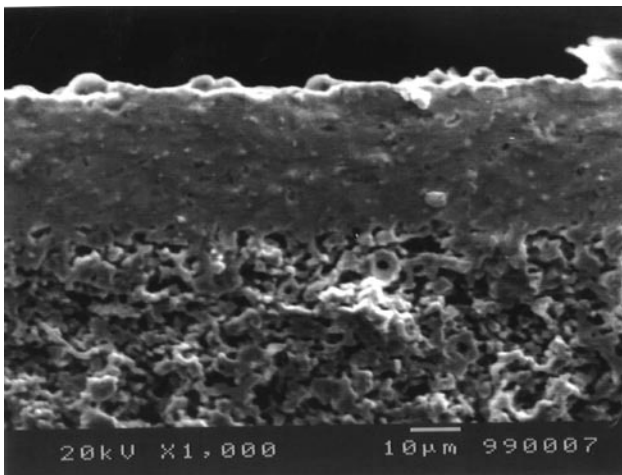 rate at lower temperatures. For applications at <850°C, we are investigating Sr-Fe-Ti oxide (SFT) membranes that do not experience a phase transition like that of SFC2. Figure 3 compares the hydrogen production rates of SFT and SFC2 membranes with similar thickness ($\approx$1 mm). The hydrogen production rate for SFC2 is the highest above 850°C, but it is much smaller below 850°C due to its phase transition. Among the SFT membranes tested, SFT2 gives the highest hydrogen production rate. To better understand the effect of Ti-doping on the hydrogen production rate, detailed studies of the electrical conductivity of SFT membranes are necessary.

Conclusions and Future Directions

Reducing the thickness of OTMs can significantly increase their hydrogen production rate if they are coated with porous layers that minimize limitations from surface reaction kinetics. To fully exploit the potential of SFC2 membranes, porous surface layers must be added to membranes with thickness <0.05 mm. We will further investigate SFC2 thin films on Ni/CGO porous substrates to better understand why their hydrogen production rates have been lower than expected to this point. We will measure the hydrogen production rate of SFC2 thin films on porous SFC2 substrates. We will continue studying alternative mixed oxygen ion/electron conductors (e.g., various SFT compositions) that do not experience a phase transition like that of SFC2. We will study the effect of SFT's titanium content on its transport properties and will test the performance of SFT cermet membranes. After the OTM's hydrogen production rate has been optimized, we will test its performance in the reforming of renewable liquid fuels such as ethanol and bio-oil and other carbon-containing fuels.
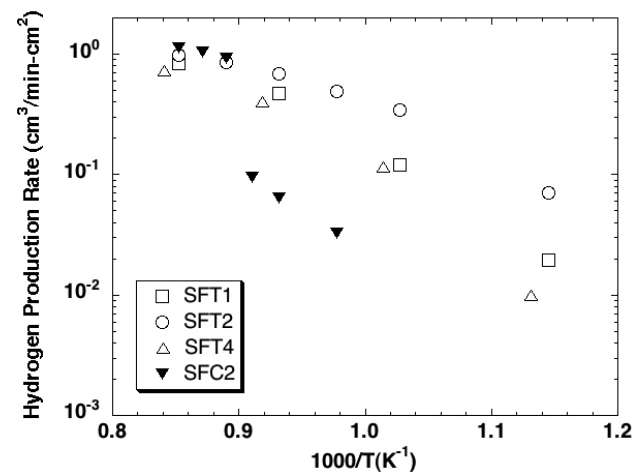

FIGURE 2. Fracture Surface of SFC2 Thin Film on Porous SFC2 Substrate

FIGURE 3. H_2 Production Rate of SFT and SFC2 Membranes (Thickness $\approx$1 mm) using Wet N_2 (pH_2O=0.03 atm) on the Hydrogen-Production Side and 4% H_2/Balance He on the Oxygen-Permeate Side

Special Recognitions & Awards/Patents Issued

1. Hydrogen Production by High-Temperature Water Splitting Using Electron-Conducting Membranes, U.S. Patent 7,087,211, Aug. 8, 2006.

FY 2007 Publications/Presentations

1. Hydrogen Production by Water Dissociation Using Mixed Conducting Dense Ceramic Membranes, Intl. J. of Hydrogen Energy, <u>32</u>, 451 (2007).

2. Reforming of Natural Gas via Water Splitting using Dense Ceramic Membranes, presented at Natl. Hydrogen Assoc. Meeting, March 19–22, 2007, San Antonio, TX.