

II.A.14 Distributed Reforming of Renewable Liquids via Water Splitting Using Oxygen Transport Membrane (OTM)

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Project End Date: Project continuation and
direction determined annually by DOE

Objectives for Fiscal Year 2008

- Enhance performance of thin (<0.1 mm) OTMs by controlling their surface microstructure.
- Evaluate chemical stability of OTMs in short-term (≤ 100 h) exposure to reaction conditions.
- Perform preliminary tests to check feasibility of reforming ethanol using OTM to split water.
- Perform preliminary H₂A analysis for reforming ethanol using OTM.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.4) 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
- (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 technical targets:

Production Unit Energy 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/gasoline gallon equivalent (gge) (delivered) at the pump by 2015 for NG
- \$3.80/gge (delivered) at the pump by 2012 for bio-derived liquids
- <\$3.00/gge (delivered) at the pump by 2017 for bio-derived liquids

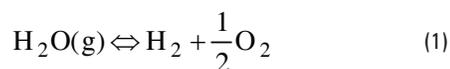
Accomplishments

- An SrFeCo_{0.5}O_x(SFC2) thin film gave the highest hydrogen production rate to date for an Argonne OTM, 17.4 cm³/min-cm².
- A preliminary test demonstrated the ability to reform ethanol using a self-supported SFC2 tube to produce hydrogen by water splitting.
- The hydrogen production rate of a self-supported SFC2 tube was stable for >700 h under various reaction conditions, including ethanol reforming.
- A preliminary H₂A analysis using the hydrogen production rate measured with Argonne's OTM predicted a total cost of \$3.31/kg hydrogen for a plant that would produce 1,500 kg H₂/day.



Introduction

The dissociation of water, shown by reaction (1), generates very low concentrations of hydrogen and oxygen even at high temperatures (e.g., 0.1% hydrogen and 0.042% oxygen at 1,600°C), because the equilibrium constant for dissociation is small.



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 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 membrane's electron and oxygen-ion conductivities, its surface oxygen exchange kinetics, and the oxygen partial pressure ($p\text{O}_2$) gradient across the membrane. Placing steam on one side of the OTM and a vaporized renewable liquid fuel on the other side establishes a large $p\text{O}_2$ gradient and makes a high hydrogen production rate possible. In this way, the OTM couples the water splitting and fuel reforming reactions, with the fuel establishing the $p\text{O}_2$ gradient that drives water splitting and the oxygen from water splitting being used in fuel reforming. The purpose of this project is to develop an OTM that can economically produce hydrogen by coupling water splitting and fuel reforming reactions.

In order to cost-effectively produce hydrogen by water splitting, an OTM must satisfy several requirements. First, it must provide a high hydrogen production rate. An OTM's hydrogen production rate increases as the OTM thickness decreases, but surface reaction kinetics can limit the hydrogen production of thin ($< \approx 0.5$ mm) OTMs. To increase the hydrogen production rate of SFC2 thin films, we enhanced the surface reaction kinetics by modifying the surface microstructures. During FY 2008, we modified the sintering conditions of SFC2 thin films to further control their microstructure and achieve a record-high hydrogen production rate for an Argonne OTM, $17.4 \text{ cm}^3/\text{min}\cdot\text{cm}^2$. OTMs must also be chemically and mechanically stable for extended periods under severe reaction conditions, and they must be available in a shape that has a large active area, e.g., tubes. This report gives results from measuring the hydrogen production rate of a self-supported SFC2 tube over a period of several hundred hours as a first step in demonstrating SFC2's chemical stability under the conditions for ethanol reforming, and it shows the microstructure of thin-film OTM tubes that are expected to give a higher hydrogen production rate. Results are also given from a preliminary H2A analysis that predicts the cost of hydrogen produced using an OTM with the water spitting reaction.

Approach

In order for an OTM to produce hydrogen cost-effectively, it must efficiently transport the oxygen produced by water splitting. To do so, the OTM must have an appropriate combination of electronic and ionic conductivity; therefore, conductivity measurements are used to identify promising membrane materials. The hydrogen production rate is measured for materials that have sufficient conductivity ($>10^{-1} \text{ ohm}^{-1}\cdot\text{cm}^{-1}$). During hydrogen production measurements, a reactive gas is used to drive the removal of oxygen by establishing an oxygen partial pressure ($p\text{O}_2$) gradient across the membrane. In order to increase the hydrogen production rate, we decrease the membrane thickness and modify membranes to overcome limitations from surface reaction kinetics. We coat OTMs with porous layers to increase the membrane's active area, and we manipulate the membrane's microstructure. Catalysts will be used to promote reactions. We measure the hydrogen production rate under various reaction conditions to evaluate the chemical stability of OTMs, because the membranes must be stable for extended periods to produce hydrogen cost-effectively. Because OTMs must be available in a shape that has a large surface area, e.g. tubes, we fabricate small tubular OTMs and test their performance. We initially fabricate small (length < 3 in.) tubes, but we will scale-up to longer (length ≈ 6 in.) OTM tubes. H2A analysis will be done to determine the cost of producing hydrogen by distributed reforming of ethanol using an OTM to split steam and provide oxygen for reforming.

Results

The microstructure and properties of SFC2 thin films are strongly influenced by the atmosphere in which they are sintered. An SFC2 film (thickness $\approx 30 \mu\text{m}$) sintered in air gave a hydrogen production rate of $\approx 6.5 \text{ cm}^3/\text{min}\cdot\text{cm}^2$, whereas a much thicker SFC2 disk (thickness $\approx 210 \mu\text{m}$) sintered in 200 ppm H_2 /balance N_2 gave a rate of $\approx 7.5 \text{ cm}^3/\text{min}\cdot\text{cm}^2$. Samples sintered in ambient air had big ($> 5\text{-}10 \mu\text{m}$) plate-like crystals, but samples sintered in 200 ppm H_2 had small ($1\text{-}2 \mu\text{m}$) equiaxed grains. Combining the microstructural observations with the hydrogen production rates suggests that a finer, equiaxed microstructure yields a higher hydrogen production rate. Figure 1 shows hydrogen production rate at 900°C versus partial pressure of water ($p\text{H}_2\text{O}$) on the steam side of an SFC2 film (thickness $\approx 25 \mu\text{m}$) on a porous SFC2 substrate after sintering in 200 ppm H_2 /balance N_2 . With $p\text{H}_2\text{O} = 0.69 \text{ atm}$, the film gave the highest hydrogen production rate to date for an Argonne OTM, $17.4 \text{ cm}^3/\text{min}\cdot\text{cm}^2$.

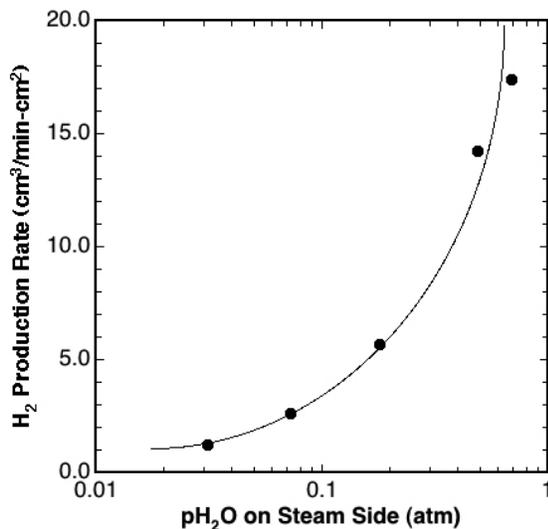


FIGURE 1. H₂ production rate at 900°C vs. pH₂O on steam side of ≈25-μm-thick SFC2 film supported by porous SFC2 substrate using 80% H₂/balance He on oxygen-permeate side of film.

To check the feasibility of reforming renewable liquid fuels while using an OTM to produce hydrogen through water splitting, we measured the hydrogen production rate of an SFC2 tube while flowing humidified N₂ on the steam side and He (0.05 atm ethanol) on the oxygen-permeate side. The tube had an outside diameter of ≈1.3 cm, length of ≈7 cm, and wall thickness of ≈0.7 mm. The total hydrogen production rate (i.e., the sum of the hydrogen production rates on the ethanol-reforming and water-splitting sides of the tube) increased as pH₂O increased on the water splitting side of the tube (Figure 2), because the increase in pH₂O shifted the water splitting equilibrium toward dissociation. To test the tube's chemical stability, we first measured its hydrogen production rate for ≈100 h at 900°C under "ethanol-reforming conditions" in which we flowed N₂ (0.03 atm H₂O) on its steam side and He (0.05 atm ethanol) on its oxygen-permeate side. The hydrogen production rate was then measured with highly reducing gas (100% CO) on the oxygen-permeate side, and then with gas that contained a high concentration of CO₂, before it was measured again under ethanol reforming conditions. After >700 h of testing under these various conditions, the hydrogen production rate during ethanol reforming was unchanged from its initial value, indicating that SFC2 had remained stable.

Although the SFC2 tube appeared chemically stable and gave a significant hydrogen production rate during the ethanol reforming experiment (Figure 2), its lack of porous surface layers and its relatively thick (≈0.7 mm) walls limited its hydrogen production rate. To increase the hydrogen production rate of OTM tubes, we are developing methods to reduce the thickness of the dense OTM layer to ≤25 μm. In one approach, we first

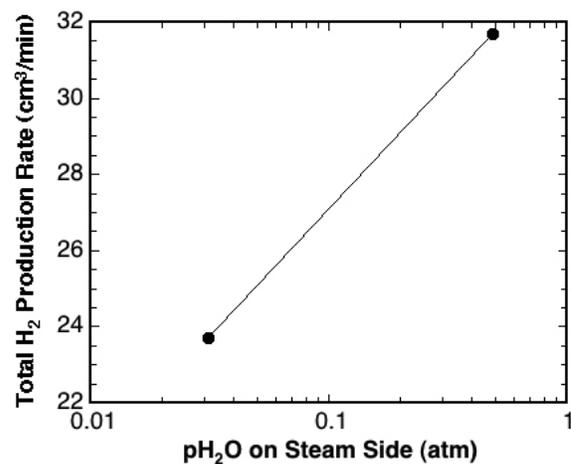


FIGURE 2. Total H₂ production rate for SFC2 tube during ethanol reforming at 900°C with humidified N₂ on steam side and He (0.05 atm ethanol) on oxygen-permeate side.

produce a porous SFC2 support tube in a cold isostatic press and pre-sinter it at 950°C for 5 h in ambient air to provide the tube with sufficient mechanical strength for subsequent handling. The outside surface of the pre-sintered tube is then painted with a paste containing SFC2 powder, which is sintered at 1,200°C in 100 ppm H₂/N₂ for 10 h. Tubes presently being made by this method (Figure 3) are typically 8-10 cm in length with an outside diameter of ≈1 cm and a membrane thickness of 25-50 μm.

Regardless of its technological feasibility, the proposed process must be economically attractive in order to be useful. In order to begin assessing the cost effectiveness of using an OTM to produce hydrogen by water splitting, a preliminary H₂A analysis was completed. The cost of hydrogen was calculated in terms of production cost, including the cost of ethanol, and total cost for plants with production capacities in the range of 250-1,500 kg H₂/day. Figure 4 breaks down the cost for producing hydrogen by ethanol reforming using OTMs in a plant that would produce 1,500 kg H₂/day. For such a plant, the total cost of hydrogen is estimated to be \$3.31/kg H₂.

Conclusions and Future Directions

Significant progress was made in FY 2008 toward demonstrating the feasibility of using dense OTMs to economically produce hydrogen by reforming ethanol via water splitting:

- A new record-high hydrogen production rate, 17.4 cm³/min-cm², was achieved.
- Experimental results confirm that hydrogen can be produced by using an OTM to couple ethanol reforming and water splitting reactions.

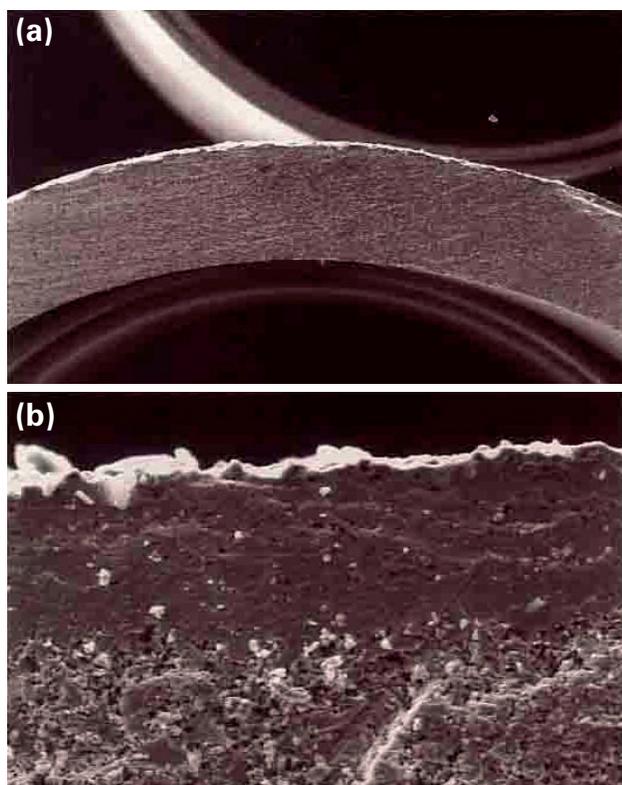


FIGURE 3. SFC2 thin film on porous tubular SFC2 support: a) cross-sectional view at “low” magnification, and b) cross-sectional view at “high” magnification.

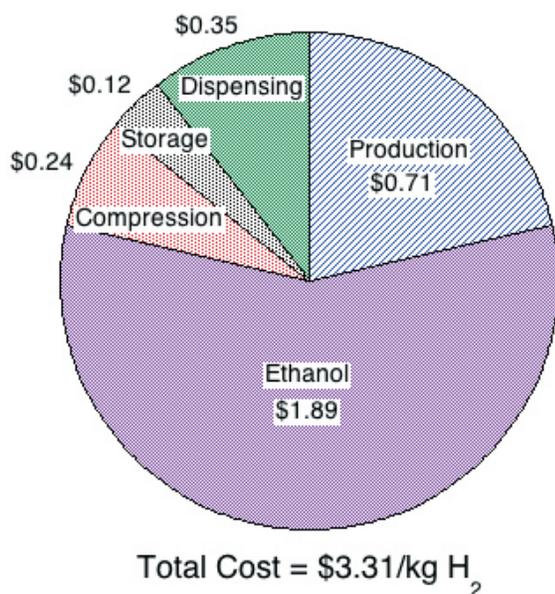


FIGURE 4. Preliminary breakdown of costs for producing hydrogen by ethanol reforming using an OTM for a plant that would produce 1,500 kg H₂/day.

- An SFC2 tube was stable for >700 h under various fuel reforming reaction conditions.
- A total cost of \$3.31/kg H₂ was predicted for a plant that would produce 1,500 kg H₂/day.

Despite the significant progress made during FY 2008, efforts are needed in several areas to fully develop the potential for producing hydrogen with OTMs. These efforts include:

- Develop OTM materials that exhibit an acceptable hydrogen production rate at low temperatures (<700°C).
- Test OTMs for hydrogen production at low temperatures (<700°C) compatible with ethanol reforming.
- Evaluate long-term chemical stability of OTM by measuring hydrogen production rate for up to ≈1,000 h during reforming of ethanol.
- Reform ethanol using OTM in presence of catalyst to enhance ethanol reforming and more efficiently drive oxygen removal from the water splitting side of the OTM.
- Develop techniques to form gas-tight seals between the membrane and metal/alloy structures.
- Improve techniques for fabricating dense thin (≤25 μm) OTM films, and apply technique to fabrication of thin-film OTM tubes.
- Provide updated hydrogen production rates to refine H2A analysis of process.

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 2008 Publications/Presentations

1. 2008 DOE Hydrogen Program Annual Merit Review & Peer Evaluation, Presentation #PDP22, Washington, D.C., June 9–13 (2008).
2. Distributed Reforming of Renewable Liquids using an OTM, DOE Hydrogen Program FY 2008 2nd Quarter report, June 2008.
3. Hydrogen Production by Water Dissociation using Oxygen Transport Membranes, presented at 213th Electrochemical Society meeting, Phoenix, AZ, May 18-23, 2008.
4. La_{0.7}Sr_{0.3}Cu_{0.2}Fe_{0.8}O_{3-x} as Oxygen Transport Membrane for Producing Hydrogen via Water Splitting, presented at 213th Electrochemical Society meeting, Phoenix, AZ, May 18-23, 2008.

5. Development of Dense Membranes for Hydrogen Production and Purification, presented at American Ceramic Society's Materials Innovations in an Emerging Hydrogen Economy meeting, Cocoa Beach, FL, Feb. 24-27, 2008.

6. Distributed Reforming of Renewable Liquids using an OTM, DOE Hydrogen Program FY 2008 1st Quarter report, Jan. 2008.

7. Hydrogen Production by Reforming of Natural Gas via Water Splitting using Dense Ceramic Membranes, presented at Intl. Symposium on Materials Issues in a Hydrogen Economy, Richmond, VA, Nov. 12-15, 2007.

8. Distributed Reforming of Renewable Liquids via Water Splitting using OTM, presented at Bio-Derived Liquids Working Group (BILIWG) Mtg., Columbia, MD, Nov. 6, 2007.