II.A.5 Distributed Reforming of Renewable Liquids via Water Splitting Using Oxygen Transport Membrane (OTM)

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direction determined annually by DOE

Objectives

Develop OTM reactor that meets DOE 2017 cost target of <$3.00/gge for producing hydrogen by reforming renewable liquids. Specific objectives for Fiscal Year 2009 were:

- Test OTMs for hydrogen production at temperatures compatible with ethanol (EtOH) reforming.
- Evaluate chemical stability of OTM during reforming of ethanol.
- Show the feasibility of 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 (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 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:	72% (lower heating value, LHV) by 2012
	65-75% (LHV) by 2017
Production Unit Capital Cost (un-installed):	$1.0M by 2012
	$600K by 2017
Total Hydrogen Cost:	$3.80/gge (delivered) at the pump by 2012
	<$3.00/gge (delivered) at the pump by 2017

Accomplishments

- Developed alternative OTMs, LSCF7328 (La-Sr-Cu-Fe-O) and SFT (Sr-Fe-Ti-O), that are suitable for ethanol reforming at low temperatures (≤700°C).
- Increased oxygen transport rate of OTMs suitable for ethanol reforming at low temperatures (≤700°C) by developing methods to fabricate the OTMs as thin films.
- Demonstrated chemical stability of LSCF7328 OTM during ≈190 h of ethanol reforming (≈6% EtOH in carrier gas) at 700-900°C.
- Analyzed ethanol conversion by OTM process at 700°C using air and steam as independent sources of oxygen for reforming.

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Introduction

The goal of this subtask is to develop dense ceramic membranes that provide oxygen for the efficient and economical production of hydrogen through the reforming of renewable liquid fuels such as EtOH and bio-oil. An OTM can be used to supply high-purity oxygen from air or from oxygen produced via water dissociation. By removing oxygen as steam dissociates, an OTM enriches the retentate in hydrogen while it supplies oxygen for reforming renewable liquid fuels on the permeate side of the membrane. In this way, water splitting can produce significant amounts of hydrogen at moderate temperatures (500-900°C). Using steam as the oxygen source, however, requires an input of energy for water dissociation. That is one factor that favors using air as the source of oxygen for reforming with an

OTM. On the other hand, using steam allows hydrogen to be produced on both sides of the OTM. To determine which source of oxygen is the most cost- and energy-effective, a detailed system analysis must be done. In this project, we are generating the necessary data for the analysis.

Approach

In order for our approach to be cost-effective in reforming renewable liquids, an OTM must efficiently transport oxygen with either air or steam as the oxygen source. Efficient oxygen transport requires the OTM to have an appropriate combination of electronic and ionic conductivity; therefore, conductivity measurements are used to identify promising membrane materials. If a material has sufficient conductivity ($>10^{-1}$ ohm^{-1}-cm^{-1}), we measure its hydrogen production rate, which is directly related to its oxygen transport rate. In order to increase the oxygen transport rate, we decrease the OTM's thickness, coat it with porous layers to increase its active area, and modify its microstructure to overcome limitations from surface reaction kinetics. Catalysts will be used to promote reforming reactions. We measure the hydrogen production rate under various reaction conditions for periods up to $\approx$1,000 h to evaluate the chemical stability of OTMs, because OTMs must be stable for extended periods to cost-effectively produce hydrogen. Because OTMs must be available in a shape with a large surface area, e.g. tubes, we fabricate small tubular OTMs and test their performance. Using steam as the oxygen source for reforming requires an energy input for water dissociation but it allows hydrogen to be produced on both sides of the OTM. In this project, we are generating the data for an independent party to conduct a detailed system analysis to determine the most cost- and energy-effective oxygen source.

Results

To make OTMs useful at temperatures compatible with reforming renewable liquids, we are developing OTMs with suitable oxygen transport rates at low temperatures ($<$700°C). Although SFC2 gives the highest oxygen transport rate (17.4 cm^3/min-cm^2) at 900°C, a phase transition dramatically decreases its oxygen transport below $\approx$825°C. LSCF7328 and SFT compositions have been identified as promising alternatives to SFC2. To compare the oxygen transport rates of various OTMs, we measure the rate at which hydrogen is produced by water splitting when steam flows on one side of the OTM and gas with a known hydrogen concentration flows on the other side, the so-called oxygen-permeate side. In this experiment, the OTM's oxygen transport rate is directly related to the hydrogen production rate on the steam side of the membrane.

Figure 1 compares the hydrogen production rate versus temperature for small disks of LSCF7328 and SFC2 with humidified N$_2$ (pH$_2$O = 0.49 atm) on the steam side of the membrane and 80% H$_2$/balance He on the oxygen-permeate side. At high temperatures, the hydrogen production rate of SFC2 is nearly as high as that of LSCF7328 despite the much greater thickness of the SFC2 membrane. Below $\approx$825°C, however, SFC2's hydrogen production rate drops by almost two orders of magnitude, making it unsuitable for use in this temperature range, whereas LSCF7328 shows a much more gradual decrease in hydrogen production rate.

Reducing an OTM's thickness increases its oxygen transport rate if surface reaction kinetics are not rate-limiting; therefore, we developed methods to fabricate thin-film LSCF7328 membranes on porous LSCF7328 substrates. The substrates provide structural support and enhance surface reaction kinetics. To assess the effect of porosity in the substrates, some substrates were prepared from LSCF7328 powder mixed with 20 wt% carbon while others were made without carbon. Thin films were prepared by painting porous LSCF7328 substrates with a slurry containing LSCF7328 powder, and then drying the sample at 80°C for 1 h and sintering at 1,100-1,140°C for 10 h in air. To gauge the effect of porous Pt on the surface reaction kinetics, Pt paste was painted on the surface of some thin films and fired at 850°C for 30 min in air.

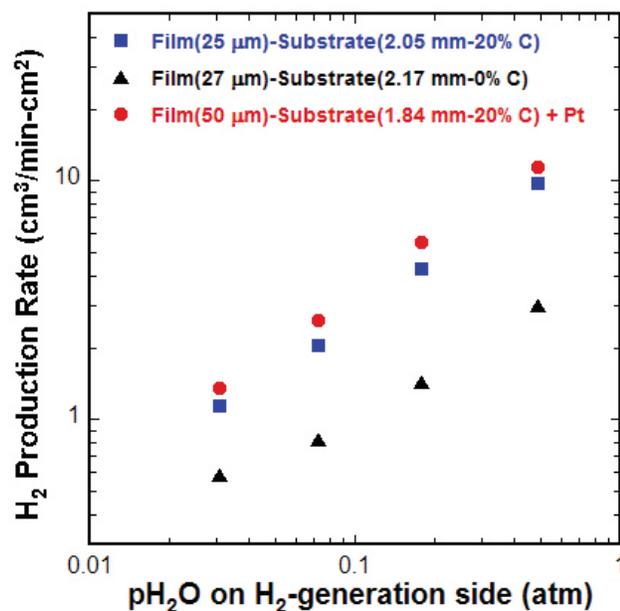Figure 2 plots the hydrogen production rate of three LSCF7328 thin films versus pH$_2$O on the steam side.
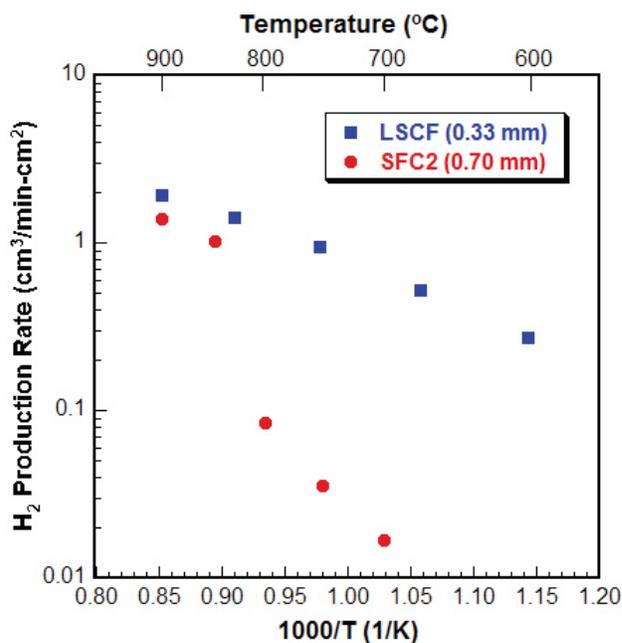
FIGURE 1. H$_2$ production rate of LSCF7328 and SFC2 disks with pH$_2$O = 0.49 atm on steam side and 80% H$_2$/balance He on oxygen-permeate side. Inset gives membrane thickness.

The substrates for two films were made with carbon powder (20 wt%) to increase their porosity, whereas the third film was prepared on a substrate made without carbon powder. Before they were coated with films, all substrates were fired in air for 10 h at 1,050°C. After firing, the substrate made without carbon powder was semi-porous with a relative density of 82.4%, whereas substrates made with carbon powder had a relative density of 51.2%. Of the films on substrates made with carbon, one was coated with a porous Pt layer, and one was not.

The porosity of substrates strongly affects the hydrogen production rate of LSCF7328 thin films (Figure 2). For the films without porous Pt, the hydrogen production rate for $pH_2O = 0.5$ atm was 3.0 cm^3/min-cm^2 on the denser (82.4% dense) substrate, but was 9.8 cm^3/min-cm^2 on the more porous (51.2% dense) substrate. The film on a porous substrate that was coated with porous Pt had an even higher hydrogen production rate (11.4 cm^3/min-cm^2), even though the film was considerably thicker (50 μm vs. ≈25 μm) than the un-coated film. This finding suggests that higher hydrogen production rates might be obtained by other enhancements of the surface reaction kinetics, e.g., by coating the films with porous layers of LSCF7328.

Ethanol reforming was studied at 700-900°C with two LSCF7328 thin-film disks and either air or water as the oxygen source. The ethanol partial pressure was fix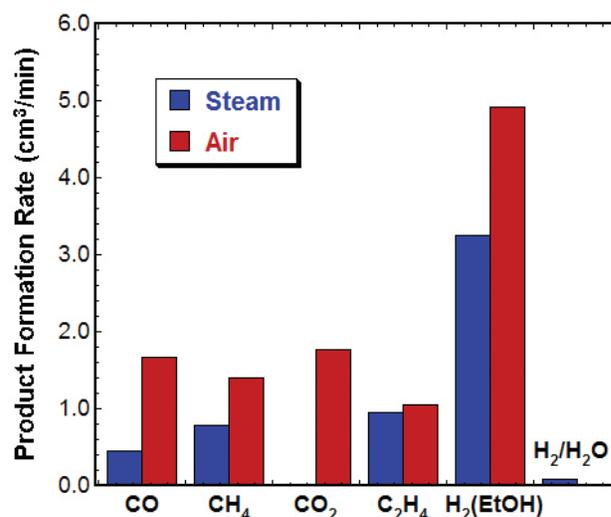ed at 0.076 atm on one side of the sample by bubbling ultra-high purity He or N_2 through absolute ethanol at 25°C at either a "low" (200 ml/min) or "high" flow rate (800 ml/min). Either air or humidified N_2 (0.49 atm H_2O) was flowed (200 ml/min) on the opposite side of the sample. Ethanol reforming was done first at 900°C for ≈140 h and then at 700°C for ≈50 h. The products included CO, CH_4, CO_2, C_2H_4, H_2, and a trace of C_2H_6. Un-reacted ethanol, water, and an unidentified component were also detected in the product stream, but ethanol and water were not always quantified because they were typically removed with an ice trap to prevent their condensation in the gas chromatograph. The unidentified peak could not be quantified due to its unknown origin, but we believe that it results from acetaldehyde, an idea that we will test with an acetaldehyde-bearing standard gas.

Figure 3 plots the results from ethanol reforming at 700°C. The CO_2 formation rate was negligible when water was the oxygen source, but it was considerable when air was the oxygen source. Using air, the CO_2 formation rate for one sample decreased as the flow rate increased, but it increased slightly for the other sample. Deposition of coke during the experiments might partly explain differences between the two samples, because time becomes a factor if coke deposition is involved, and the timing and sequence of measurements were not identical for the samples.

Based on the coke formation and the observed analytical results, several changes will be made in future tests. First, we will increase the water/ethanol ratio in the feed in order to reduce coke formation. Second, we will deposit a rhodium-based catalyst on the OTM in order to enhance the reaction rate between carbon-bearing species, such as CO and CH_4, and

FIGURE 2. H_2 production rate at 900°C vs. pH_2O on steam side of LSCF7328 thin films on LSCF7328 substrates made with 20% carbon (51.2% dense) or without carbon (82.4% dense). Inset gives film/substrate thicknesses. 80% H_2/balance He was flowed on oxygen-permeate side.

FIGURE 3. Products formation rates during ethanol reforming at 700°C with LSCF7328 thin-film OTM with He or N_2 (0.076 atm EtOH) flowing at a rate of 800 ml/min on one side of sample and air or humidified N_2 (0.49 atm H_2O) flowing at a rate of 200 ml/min on other side.

oxygen supplied by the membrane, while minimizing the reaction between hydrogen and oxygen. Third, we will increase the active area of the OTM in order to increase the supply of oxygen during ethanol reforming. The effect of the OTM was not large in the initial tests, because the OTM's active area was small (≈ 1.27 cm^2). In the future, we will test OTM tubes with much larger active area (>10 cm^2).

Conclusions and Future Directions

Significant progress was made in FY 2009 toward demonstrating the feasibility of using dense OTMs to economically produce hydrogen by reforming ethanol. Future directions include:

- Test OTMs for hydrogen production at temperatures compatible with ethanol reforming.
- Study effects of ethanol concentration, gas flow rates, OTM thickness.
- Employ catalysts to enhance the reforming of ethanol and oxygen transport.
- Generate necessary data for H2A analysis using air and steam as the oxygen source.
- Have a third party perform detailed cost analysis to judge which oxygen source (air or steam) is more cost- and energy-effective.
- Evaluate chemical stability of the OTM for up to $\approx 1,000$ h during ethanol reforming at temperatures in range 550-800°C.
- Select OTM composition(s) and reaction conditions.
- Test ethanol reforming with longer OTM tubes and define suitable reforming conditions.

FY 2009 Publications/Presentations

1. Distributed Reforming of Renewable Liquids Using Gas Transport Membranes, DOE Hydrogen Program Annual Merit Review and Peer Evaluation Meeting, May 18–22, 2009. (http://annualmeritreview.energy.gov)