

II.A.5 Distributed Reforming of Renewable Liquids Using Oxygen Transport Membranes

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

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 EtOH 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/gasoline gallon equivalent (gge) (delivered) at the pump by 2012
 - <\$3.00/gge (delivered) at the pump by 2017

A preliminary techno-economic analysis estimated a cost of ≈\$3.40/gge for producing hydrogen by reforming EtOH with an OTM. DOE's hydrogen cost target is being revised at the present.

Objectives

Develop a compact ceramic membrane reactor that meets the DOE 2017 cost target for producing hydrogen by reforming renewable liquids. Specific objectives for Fiscal Year (FY) 2010 were:

- Use oxygen transport membrane (OTM) to reform ethanol (EtOH) at ≤700°C.
- Generate data for detailed analysis to assess benefits of approach.

Technical Barriers

This project addresses the following technical barriers from the Production section (3.1.4) of the Fuel Cell 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
- (P) Flux
- (R) Cost

Accomplishments

- Significantly increased EtOH conversion with a new OTM, but analysis of the products of reforming indicated that a suitable catalyst is needed in order to increase hydrogen production during reforming.
- Enhanced H₂ production rate by increasing EtOH concentration and H₂O/EtOH in feed during EtOH reforming with OTM.
- Developed BFZ1 (BaFe_{0.9}Zr_{0.1}O_x) a new OTM whose significantly higher oxygen flux might enhance EtOH conversion at low temperature (≈500°C).
- Provided data to Directed Technologies, Inc. (DTI), whose preliminary analysis indicated a hydrogen production cost of ≈\$3.40/gge for a station capacity of 1,500 kg H₂/day.



Introduction

Previous study has shown that supplying oxygen with an OTM reduced the costs of methane reforming by ≈ 30 -40% and energy consumption by ≈ 30 %. Similarly, it has been shown that supplying oxygen during EtOH reforming increases EtOH conversion and enhances catalyst performance by preventing coke formation [1]. An OTM can supply high-purity oxygen for EtOH reforming by separating it from air without using a separate gas separation unit. Because the OTM is a mixed conductor, the oxygen transport requires neither electrodes nor external power circuitry, i.e., the process is non-galvanic. The oxygen flux through the membrane depends on the membrane's electron and oxygen-ion conductivities, its surface oxygen exchange kinetics, and the oxygen partial pressure (pO_2) gradient across the membrane.

The goal of this subtask is to develop a dense OTM that provides oxygen for efficiently and economically producing hydrogen through the reforming of renewable liquid fuels such as EtOH and bio-oil. Using an OTM to supply high-purity oxygen from air can reduce the cost and energy consumption associated with EtOH reforming, but a detailed system analysis must be done to determine the cost and energy benefits. In this project, we are generating data for the system analysis. While generating the necessary data, we are also developing OTMs that transport oxygen at an industrially significant rate at low temperature ($\approx 500^\circ\text{C}$) and possess sufficient mechanical and chemical stability to withstand the large stresses that develop from having air on one side of the OTM and carbonaceous fuels on the other side.

Approach

In order for our approach to be cost-effective in reforming renewable liquids, an OTM must efficiently transport oxygen. In order to efficiently transport oxygen, an OTM must have an appropriate combination of electronic and ionic conductivity; therefore, we use conductivity measurements to identify promising membrane materials. If a material has sufficient conductivity ($>10^{-1} \text{ ohm}^{-1}\text{-cm}^{-1}$), we measure its hydrogen production rate, which is directly related to its oxygen transport rate. In order to increase the oxygen transport rate, we adjust the OTM's composition, decrease its 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. In order to evaluate the expected cost and energy benefits of reforming renewable liquids with an OTM, we are generating the necessary data for an independent party, Directed Technologies, Inc., to conduct a detailed system analysis.

Results

OTMs made of $\text{La}_{0.7}\text{Sr}_{0.5}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_x$ (LSCF), $\text{Sr}_{0.1}\text{Fe}_{0.9}\text{Ti}_{0.10}\text{O}_x$ (SFT1), $\text{BaFe}_{0.975}\text{Zr}_{0.025}\text{O}_3$ (BFZ0), and BFZ1 were tested. Powders for the OTMs were prepared by conventional solid state reaction between the constituent oxides. Dense OTMs were prepared in the shape of disks, tubes, or OTM thin films on porous disks or tubes. Before measuring an OTM's oxygen flux or its hydrogen production during EtOH reforming, the OTM was tested for interconnected porosity and/or microcracks by checking if isopropyl alcohol (IPA) penetrated it. Penetration of the OTM by even a small amount of IPA was easily seen as darkening of its surface and indicated that the OTM contains cracks or interconnected porosity.

If IPA did not penetrate an OTM, it was tested on a fixture that allowed separate gases to be flowed over opposite faces of the OTM. The oxygen flux was measured while air flowed on the "feed" side of the OTM and ultra-high purity He on the "sweep" side, both gases flowing at a rate of 150 ml/min. The oxygen concentration in the sweep gas was measured with a Hewlett-Packard 6890 gas chromatograph (GC); the nitrogen concentration in the sweep gas was measured to correct for minor oxygen leakage through the gas seal. EtOH reforming was studied while feed with a steam/EtOH ratio ranging from 0/1 to 5/1 flowed on one side of the OTM, while air flowed on the opposite side. As a reference, EtOH reforming was also done with a dense, oxygen-impermeable Al_2O_3 cap instead of an OTM. The concentrations of EtOH reforming products were measured during the tests with the GC.

Figure 1 compares the compositions of the product streams during EtOH reforming at 550°C with a thin-film OTM tube (LSCF, thickness $\approx 30 \mu\text{m}$) and with a dense, oxygen-impermeable Al_2O_3 "blank". Steam was not added to the feed during these tests. The hydrogen formation rate with the OTM, although not large in this experiment without a catalyst, was more than twice that with the Al_2O_3 blank. Whereas the formation rates of CO , H_2O , and CO_2 were negligible with the blank, they all increased significantly when an OTM was used. The amount of un-reacted EtOH decreased by >50 % with an OTM, giving an EtOH conversion of ≈ 63 % as compared to the EtOH conversion of ≈ 47 % that was reported in FY 2009.

The higher formation rates for products and the smaller concentration of un-reacted EtOH clearly show

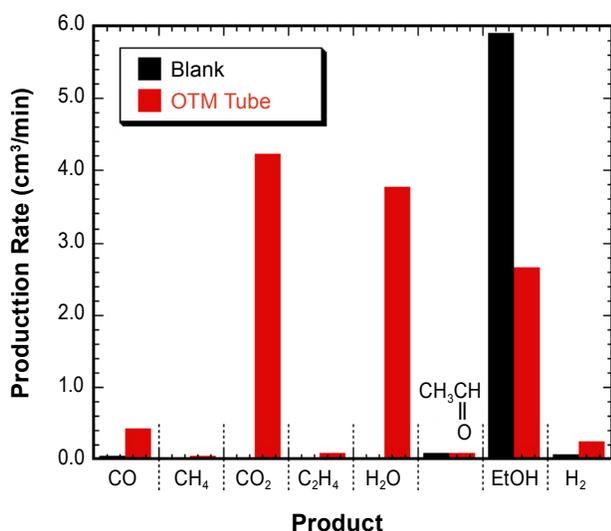


FIGURE 1. Flow rates of species in product stream during EtOH reforming experiments at 550°C with LSCF thin-film OTM tube (OTM thickness $\approx 30 \mu\text{m}$) and oxygen-impermeable Al_2O_3 blank. "EtOH" shows flow rate for un-reacted EtOH.

that oxygen supplied by the OTM enhanced EtOH reforming. The high formation rate of H_2O indicates that much of the hydrogen formed by reforming reacts with the oxygen supplied by the OTM. The high H_2O formation rate demonstrates that a catalyst is needed to promote preferential oxidation of carbon-containing products. Although the formation rate of ethylene formed by dehydration of EtOH was not high, its presence is highly undesirable because ethylene is a precursor of coke formation, and may lead to catalyst deactivation [2].

EtOH reforming with an LSCF tube (thickness $\approx 1.5 \text{ mm}$) was studied using steam/EtOH ratios up to 5/1. As before, reforming experiments were also done with oxygen-impermeable Al_2O_3 as a reference. Steam/EtOH mixtures were prepared by mixing two gas streams (N_2 or He), one saturated with EtOH at room temperature (23°C), giving $p_{\text{EtOH}}=0.067 \text{ atm}$, and the other saturated with water at a controlled temperature (38.5-72.1°C).

Figure 2 shows the effect of steam/EtOH ratio on the hydrogen formation rate. The hydrogen formation rate increased as the steam/EtOH ratio increased in both experiments. In the blank experiment, the hydrogen formation rate increased the most as the steam/EtOH ratio increased to 3/1 and only slightly more as the steam/EtOH ratio increased to 5/1. With $p_{\text{EtOH}}=0.067 \text{ atm}$, the hydrogen formation rate with the OTM tube was measured only for steam/EtOH ratios of 0/1 and 3/1. Under both conditions, the hydrogen formation rate with the OTM tube was about twice as high as that measured in blank experiments. When p_{EtOH} was increased to 0.135 atm (with a steam/EtOH

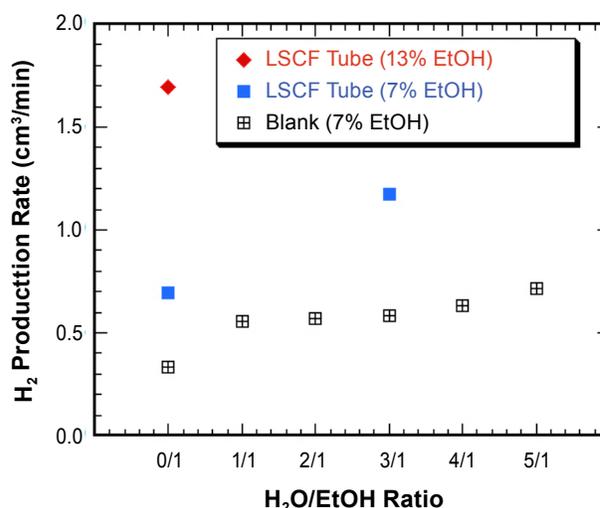


FIGURE 2. Hydrogen formation rates during EtOH reforming experiments with LSCF tube and oxygen-impermeable Al_2O_3 blank vs. steam/EtOH ratio in the feed gas.

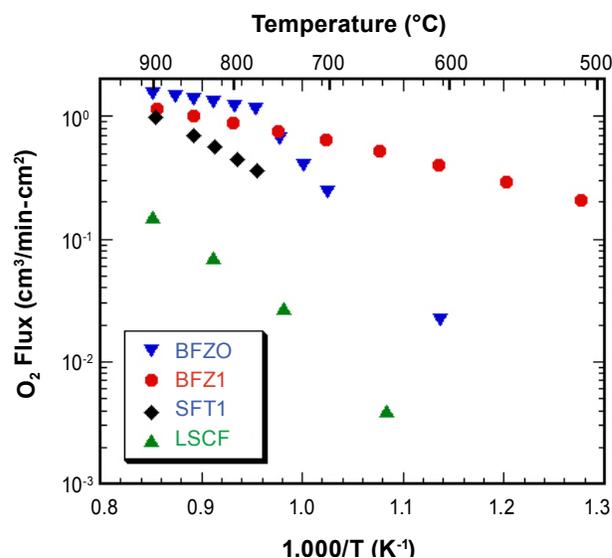


FIGURE 3. Oxygen flux (normalized for thickness of 1.0 mm) of BFZO, BFZ1, SFT1, and LSCF disks.

ratio of 0/1), the hydrogen formation rate increased to $\approx 1.7 \text{ cm}^3/\text{min}$. A blank experiment was not done with the higher p_{EtOH} .

Figure 3 shows the oxygen flux (normalized for thickness of 1 mm) versus inverse temperature for BFZO, BFZ1, SFT1, and LSCF disks. The oxygen flux of BFZ1 is about 20% higher than that of SFT1 at 900°C, and the difference in flux increases as temperature decreases. The oxygen flux of BFZ1 is one to two orders of magnitude higher than that of LSCF over the whole temperature range. With a significantly higher oxygen flux at low temperature ($\approx 500^\circ\text{C}$), BFZ1

appears promising for use during EtOH reforming at low temperature, provided that it exhibits good chemical stability during reforming.

DTI is performing a detailed techno-economic analysis of EtOH reforming with an OTM to evaluate its cost- and energy-benefits. For the analysis, Argonne is providing oxygen flux and EtOH conversion data for promising OTMs. A preliminary analysis shows that the cost of the EtOH feedstock comprises a major fraction ($\approx 70\%$) the cost of producing hydrogen by EtOH reforming with an OTM. Figure 4 shows the cost of producing hydrogen by EtOH reforming with an OTM is $\approx \$3.10$ - $\$3.60/\text{kg H}_2$, depending on the EtOH fuel efficiency. A more detailed analysis is underway.

Conclusions and Future Directions

Significant progress has been made in demonstrating that a dense OTM can enhance the reforming of renewable liquids. In order to further evaluate the benefits of this approach, we will:

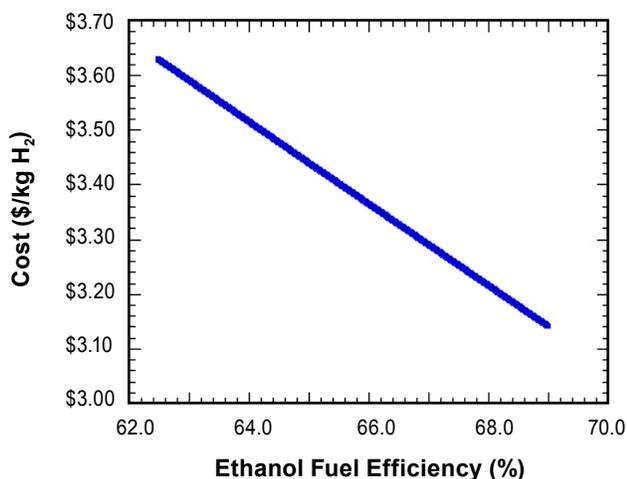


FIGURE 4. Results from preliminary analysis of cost to produce hydrogen by EtOH reforming with an OTM versus EtOH fuel efficiency. Cost estimate analysis done by DTI.

- Reform EtOH with OTM in presence of catalyst(s).
- Generate key data for performing a detailed economic analysis of our approach.
- Continue testing the performance of OTMs during EtOH reforming at $\approx 500^\circ\text{C}$.
- Study effect of EtOH concentration, gas flow rates, and OTM thickness.
- Evaluate chemical stability of OTM during reforming of EtOH.
- Work with DTI to perform a detailed cost and energy analysis to judge the merits of using OTM to enhance H_2 production by EtOH reforming.
- Compare the cost of hydrogen production by OTM-assisted EtOH reforming with conventional steam reforming.

FY 2010 Publications/Presentations

1. Reforming Natural Gas and Renewable Liquids Using Mixed-Conducting, Dense, Ceramic Membranes, presented at 217th Electrochem. Soc. Mtg., Vancouver, Canada, April 25-30 (2010).
2. Distributed Reforming of Renewable Liquids using Oxygen Transport Membranes, presented at 2010 U.S.D.O.E. Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, June 7–11, Washington, D.C.
3. Hydrogen Production from Fossil and Renewable Sources Using an Oxygen Transport Membrane, *Intl. J. Hydrogen Energy*, 35 (2010) 4103–4110.

References

1. F. Frusteri et al., *Intl. J. Hyd. Energy*, **31**, 2193-2199 (2006).
2. D.K. Liguras et al., *Appl. Catal. B*, **43**, 345 (2003).
3. K. Watanabe et al. *J. Electrochem. Soc.*, **156**, E81 (2009).