

## II.A.3 Distributed Reforming of Renewable Liquids Using Oxygen Transport Membranes (OTMs)

U. (Balu) Balachandran (Primary Contact),  
C.Y. Park, T.H. Lee, Y. Lu, J.J. Picciolo,  
J.E. Emerson, and S.E. Dorris  
Argonne National Laboratory  
9700 S. Cass Ave.  
Argonne, IL 60439-4838  
Phone: (630) 252-4250  
E-mail: balu@anl.gov

DOE Manager  
HQ: Sara Dillich  
Phone: (202) 586-7925  
E-mail: Sara.Dillich@ee.doe.gov

Subcontractor:  
Directed Technologies, Inc. (DTI), Arlington, VA

Project Start Date: May, 2005  
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/gge (delivered) at the pump by 2012 <\$3.00/gge (delivered) at the pump by 2017

A preliminary techno-economic analysis in FY 2010 estimated a cost of ≈\$3.40/gge for producing hydrogen by reforming EtOH with an OTM.

### Fiscal Year (FY) 2011 Objectives

Develop a compact ceramic membrane reactor that meets the DOE 2017 cost target of <\$3.00/gasoline gallon equivalent (gge) for producing hydrogen by reforming renewable liquids. Specific objectives for FY 2011 were:

- Use oxygen transport membrane (OTM) to reform ethanol (EtOH) at ≤700°C in presence of catalyst.
- Perform detailed Design for Manufacturing and Assembly and H2A analyses 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
- (N) Hydrogen Selectivity
- (P) Flux
- (R) Cost

### FY 2011 Accomplishments

- Significantly increased EtOH conversion using BaFe<sub>0.9</sub>Zr<sub>0.1</sub>O<sub>x</sub> (BFZ1), an OTM that gives significantly higher oxygen flux at low temperature (≈500°C), but analysis of the products indicated the need for a suitable catalyst to increase hydrogen production.
- Used Rh-based catalyst on a small (1.3 cm<sup>2</sup>) BFZ1 disk to nearly quadruple the hydrogen production rate compared to that of a much larger (15.3 cm<sup>2</sup>) lanthanum strontium cobalt iron oxide (LSCF) tube.
- Estimated a hydrogen production cost of \$3.40/kg H<sub>2</sub> for a station with a 1,500 kg H<sub>2</sub>/day capacity, (analysis by DTI).



### Introduction

Others have shown that supplying oxygen with an OTM reduced the costs of methane reforming by ≈30-40% and energy consumption by ≈30%. 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 ( $p_{O_2}$ ) 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. To assess the potential for reducing the cost and energy consumption associated with EtOH reforming, DTI performed a detailed system analysis to determine the cost and energy benefits of using an OTM to supply high-purity oxygen from air. While generating the necessary data for DTI's system analysis, we continued 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 under the large stresses that develop from having air on one side of the OTM and carbonaceous fuels on the other side.

## Approach

In order to be cost-effective during the reforming of renewable liquids, an OTM must efficiently transport oxygen. For efficient oxygen transport, 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. With promising OTMs, catalysts are 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 assess the expected cost- and energy-benefits of reforming renewable liquids with an OTM, we shared our oxygen flux data to an independent party, DTI, who conducted a detailed system analysis.

## Results

BFZ1 powder was prepared by conventional solid-state synthesis using  $\text{BaCO}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{ZrO}_2$  as starting materials. Stoichiometric amounts of starting materials were ball-milled for 1-3 days with zirconia media in isopropyl alcohol (IPA). After drying the mixture, it was heated in ambient air at  $800\text{-}850^\circ\text{C}$  for 10-20 h and then ball-milled as before for one day. The dried powder was heated again in ambient air at  $880\text{-}900^\circ\text{C}$  for 10-20 h, and then was ball-milled again.

Although the microstructure of BFZ1 thin films is acceptable, they have shown a tendency to crack during EtOH reforming conditions; therefore, an EtOH reforming experiment was done using a relatively thick (0.67 mm) BFZ1 disk. A disk (1 inch diameter) was uniaxially pressed from BFZ1 powder and was then sintered at  $1,340^\circ\text{C}$  for 10 h in 100 ppm  $\text{H}_2$ /balance  $\text{N}_2$ . To deposit Rh-catalyst on one face of the disk, rhodium nitrate ( $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ , Alfa Aesar, 99.9%) was dissolved in deionized water, and then a binder and BFZ1 powder was added to the solution. Heating the solution with binder and powder at  $<80^\circ\text{C}$  while stirring gave a viscous paste that was painted onto the surface of the BFZ1 disk. The painted disk was dried in air and installed for an EtOH reforming test at  $600^\circ\text{C}$ .

A glass ring was used to seal the Rh-coated BFZ1 disk to the test fixture by heating overnight at  $650^\circ\text{C}$  while flowing He on the Rh-catalyst side and air on the other side. After obtaining a seal at  $650^\circ\text{C}$ , the tube was cooled to  $600^\circ\text{C}$  for the EtOH reforming test. The EtOH partial pressure ( $p_{\text{EtOH}}$ ) was fixed on the Rh-coated side of the disk by bubbling ultrahigh purity He or  $\text{N}_2$  through absolute EtOH at  $23^\circ\text{C}$  ( $p_{\text{EtOH}} \approx 0.067 \text{ atm}$ ), while air was flowed on the other side of the disk. During the measurements, both gases flowed at a rate of 200 ml/min. The concentrations of products from EtOH reforming were measured with an Agilent gas chromatograph.

Figure 1 shows cross-sectional and plan views of a BFZ1 disk coated with catalyst. An EtOH reforming test with the sample shown in Figure 1 was unsuccessful, because a gas-tight seal was not made. EtOH reforming results were obtained with a second sample. The sample shown in Figure 1 was heated overnight at  $930^\circ\text{C}$ , because a gold ring was used to make a gas seal rather than a glass ring. Other than being heated to higher temperature in order to make a seal, the unsuccessful sample (Figure 1) was identical to the sample used in the successful reforming test. The porous catalyst-containing layer on top of the BFZ1 disk had a thickness of  $\approx 10 \mu\text{m}$ . The BFZ1 disk itself had several isolated pores but the pores did not appear to be interconnected.

An EtOH reforming test was conducted at  $600^\circ\text{C}$  with a Rh catalyst-coated BFZ1 disk. Table 1 summarizes the results for the BFZ1 disk coated with catalyst along with data that was the reported previously [2] for an LSCF thin-film tube not coated with catalyst. Figure 2 compares the total production rates for the products of EtOH reforming with the BFZ1 disk and the LSCF thin-film tube. Figure 3 plots the relative hydrogen production rates, i.e., the ratios of the hydrogen production rate to the production rates for the other products of reforming.

The carbon balance and EtOH conversion of BFZ1 were 90.9% and 28.0%, respectively. The EtOH conversion for the BFZ1 disk was lower than that of the LSCF thin-film tube due to the disk's smaller active area ( $\approx 1.3$  vs.  $15.3 \text{ cm}^2$ ). Despite its lower EtOH conversion and its smaller active area, the total hydrogen production rate of BFZ1 was

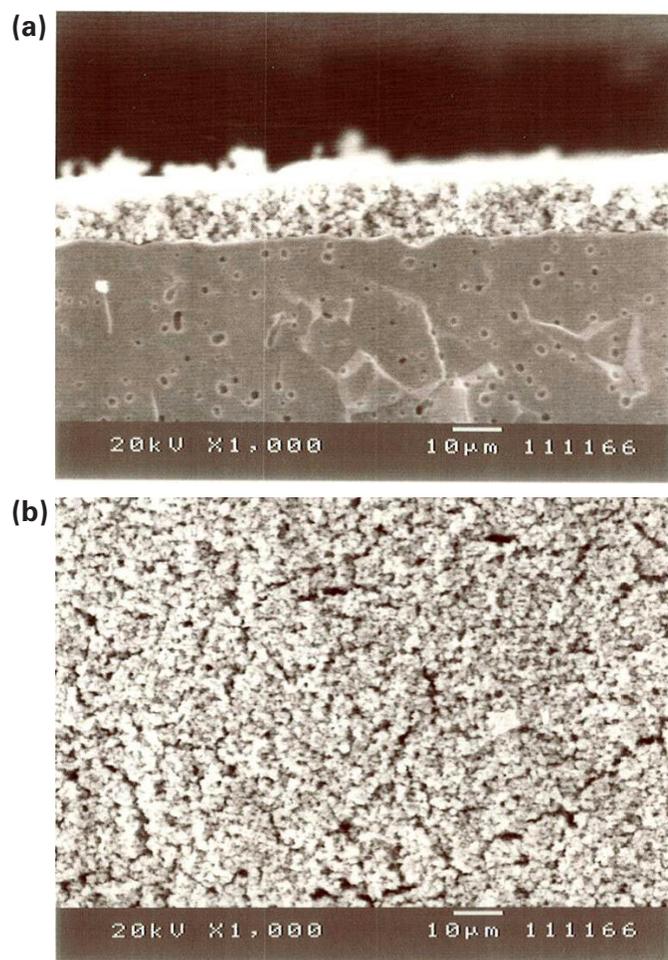


FIGURE 1. Secondary electron images of a) fracture-surface and b) plan view of Rh catalyst-coated BFZ1 disk.

TABLE 1. Results of EtOH Reforming Experiments at 600°C

OTM	EtOH Reforming Results				
	OTM Thickness	HPR* (cm <sup>3</sup> /min)	H <sub>2</sub> /Total	C Balance (%)	EtOH conversion (%)
LSCF thin-film tube	~30 μm	0.27	0.031	75.8	61.8
BFZ1 disk + Rh	0.67 mm	0.96	0.360	90.9	28.0

\* HPR = hydrogen production rate

0.96 cm<sup>3</sup>/min, which is 3.6 times higher than that of the LSCF tube. Only a small amount of coke was found after the experiment with the BFZ1 disk, an observation that is consistent with the improved carbon balance for the BFZ1 disk, compared to that for the LSCF thin-film tube.

Figure 2 shows that, in addition to its higher production rate, the BFZ1 disk gave lower production rates for the major products (CO<sub>2</sub> and H<sub>2</sub>O) from EtOH reforming

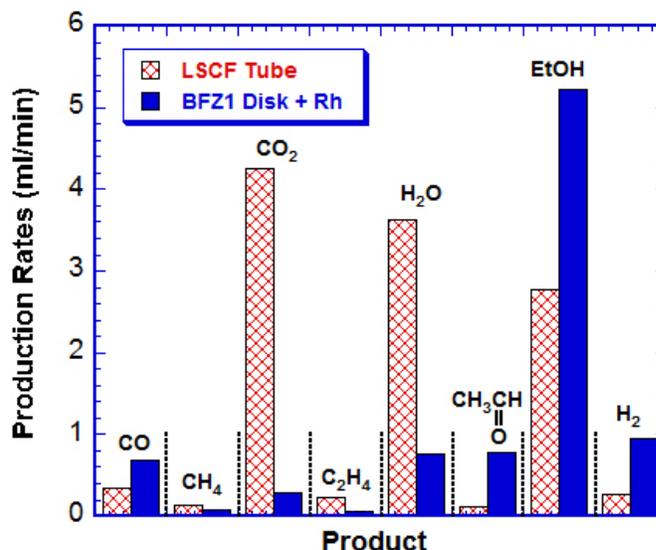


FIGURE 2. Total production rates for products of EtOH reforming at 600°C with Rh catalyst-coated BFZ1 disk (thickness=0.67 mm, active area=1.3 cm<sup>2</sup>) and LSCF tubular thin-film (thickness=0.03 mm, active area=15.3 cm<sup>2</sup>) not coated with catalyst.

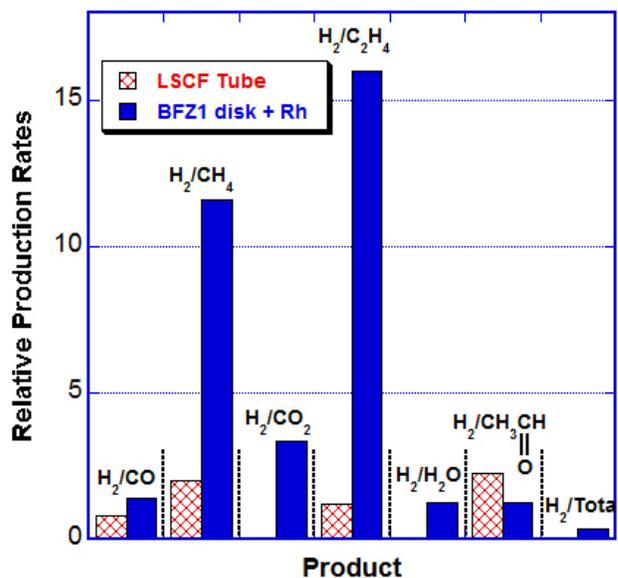


FIGURE 3. Relative production rates for products of EtOH reforming at 600°C with Rh catalyst-coated BFZ1 disk (thickness=0.67 mm, active area=1.3 cm<sup>2</sup>) and LSCF tubular thin-film (thickness=0.03 mm, active area=15.3 cm<sup>2</sup>) not coated with catalyst.

with the LSCF thin-film tube. The shift toward hydrogen production is seen more clearly in Figure 3, which plots the relative hydrogen production rates for the BFZ1 disk and LSCF tube. The catalyst-coated BFZ1 disk gave considerably higher relative hydrogen production rates for all products except acetaldehyde (CH<sub>3</sub>CHO). The ratio of the hydrogen production rate to the sum of production rates

for all other products, given by  $H_2/\text{Total}$  in Figure 3 and Table 1, was more than an order of magnitude higher for the BFZ1 disk with catalyst than for the LSCF tube without catalyst (0.360 for Rh+BFZ1 vs. 0.031 for LSCF). The results indicate that the addition of the Rh catalyst played an important role for increasing the hydrogen selectivity and decreasing coke formation.

DTI completed a detailed techno-economic analysis of EtOH reforming with an OTM to evaluate its cost- and energy-benefits. For the analysis, Argonne provided oxygen flux and EtOH conversion data for promising OTMs. The 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. The cost of producing hydrogen by EtOH reforming with an OTM was estimated to be  $\approx \$3.10$ - $\$3.60/\text{kg } H_2$ , depending on the EtOH fuel efficiency.

### Conclusions and Future Directions

Significant progress was made in demonstrating that a dense OTM can enhance the reforming of renewable liquids. In order to further evaluate the benefits of this approach, if funding becomes available to continue this work, we will:

- Continue testing the performance of OTMs during EtOH reforming at lower temperatures ( $\approx 500^\circ\text{C}$ ).
- Study effect of EtOH concentration, gas flow rates, and OTM thickness.

- Evaluate effect of Rh-catalyst during EtOH reforming using tubular OTM with larger active area ( $\approx 15 \text{ cm}^2$ ).
- Evaluate performance of other catalysts during EtOH reforming with OTM.
- Evaluate chemical stability of OTM during reforming of EtOH.
- Provide DTI with data on improved performance of OTMs to refine the cost and energy analysis and better evaluate the merits of using OTM to enhance  $H_2$  production by EtOH reforming.

### FY 2011 Publications/Presentations

1. Distributed Reforming of Renewable Liquids using an OTM, DOE Hydrogen Program FY 2011 1<sup>st</sup> Quarter report, January 2011.
2. Distributed Reforming of Renewable Liquids using an OTM, DOE Hydrogen Program FY 2011 2<sup>nd</sup> Quarter report, April 2011.

### References

1. F. Frusteri et al., *Intl. J. Hyd. Energy*, **31**, 2193-2199 (2006).
2. U. Balachandran, Distributed Reforming of Renewable Liquids using an OTM--Quarterly Report for Apr. – Jun. 2010, Argonne National Laboratory.