

II.K.3 Distributed Energy Project*

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Subcontractors:

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- University of North Dakota, Grand Forks, ND
- CTP Hydrogen, Westborough, MA

Project Start Date: September 1, 2005

Project End Date: August 31, 2008

*Congressionally directed project

Program Multi-Year Research, Development and
Demonstration Plan:

(N) Hydrogen Selectivity

(R) Cost

Technical Targets

This project is conducting fundamental studies of hydrogen separation through mixed ionic and electric conducting membranes, ceramic membranes, and the need to use the waste gas (mostly CO) via solid oxide fuel cells to make syngas a viable source of hydrogen. Insights gained from these studies will be applied toward the design and synthesis of integrated hydrogen production from syngas and syngas utilization:

- Efficiency: 70% (thermal and electric)
- Capital cost: \$1,000/kw equivalent
- Total hydrogen cost: \$3.00 per gge

Accomplishments

- Created anode materials that show 90% improvement in sulfur tolerance when H₂S concentrations reach 300 ppm in syngas.
- Created ceramic membranes capable of high selectivity for hydrogen separation in syngas.
- Completed work on chemically enhanced electrolysis of water using mixed ionic and electrically conducting membranes.

Objectives

- Investigate technology that will allow solid fuels, primarily biomass, to be used as the feedstock for distributed energy systems.
- Study of low-cost technologies for syngas separation to produce hydrogen and to use the syngas with solid oxide fuel cells.
- Create sulfur tolerant anodes in planar solid oxide fuel cells will allow high efficiency electrical production.
- Investigate inorganic membranes to produce a “pure” stream of H₂ from biomass (or coal) derived mixture.
- Investigate low-cost separations technology that can create pure hydrogen from the synthesis gas.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies



Introduction

The overall vision is to develop technology to create a viable “distributed energy” system – one that provides electricity from stationary solid oxide fuel cells, heat from the fuel cells, and useable hydrogen from the synthesis gas. The goal of this project is to create technology that will allow solid fuels, primarily biomass, to be used as the feedstock for distributed energy systems. The objectives of this proposal are the study of low-cost technologies for syngas separation to produce hydrogen and to use the syngas with solid oxide fuel cells. Specifically, the use of sulfur tolerant anodes in planar solid oxide fuel cells will allow high efficiency electrical production, while inorganic membranes will be created to produce a “pure” stream of H₂ from biomass (or coal) derived mixture. The final objective is perhaps the most critical – to investigate low-cost separations technology that can create pure hydrogen from the synthesis gas. This project attempts to create a viable

hydrogen infrastructure by using solid fuel as a source, while keeping in mind that flexibility is needed so that such a system.

Approach

The approach taken in this work was to do theoretical modeling to identify the effects of various syngas constituents on hydrogen separation, then to perform empirical tests to quantify the separation or hydrogen generation performance. Experimental conditions were typically set at a fixed temperature, utilizing simulated O₂ blown syngas, measuring electrochemical properties and hydrogen flux, or in the case of the fuel cells, area specific resistance (ASR) and power density. Material analyses on the membranes or cells (before and post tests) using scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) were done to determine if any structural or composition changes had taken place.

Results

MEIC Membrane Hydrogen Production via Chemical Electrolysis

Hydrogen can be derived from a carbonaceous fuel stream through an electrochemical process by using a membrane material that has both ionic and electronic conducting properties. The process is driven by the oxygen partial pressure difference between steam on one side of the membrane and that of the fuel on the other side. The resulting gradient in oxygen partial pressure sets up an electrochemical voltage which forms the driving potential for the process.

On the surface of the membrane steam is electrochemically reduced to hydrogen while the resultant oxygen picks up electrons and travels as an ion through the membrane (Figure 1). Once through the membrane the oxygen ion releases its electrons and oxidizes the fuel that is present on that side of the membrane. The electrons travel back to the steam side through the membrane thereby closing the circuit. The membrane is fully dense, but does allow passage of oxygen ions and electrons. Therefore the hydrogen being produced is very pure and diluted with steam only, which if required can be condensed with relative ease.

In Figure 2, the performance of the created mixed electronic and ionic conducting (MEIC) cell is shown to be reasonably stable over the test period and even appears to increase somewhat, from 1.0 ml/cm²/min initially to 1.3 ml/cm²/min at the end of the test. This ‘settling in’ phenomenon is commonly seen in fuel cell testing and due to the similarities of the processes this is not surprising. The operating temperature was held at 950°C for most of the test. Exceptions are at the start of the test and after 48 hours. At these points the

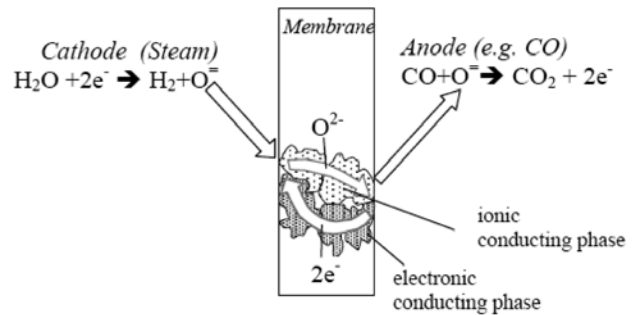


FIGURE 1. Schematic Representation of the Process of Chemically Driven Electrolysis

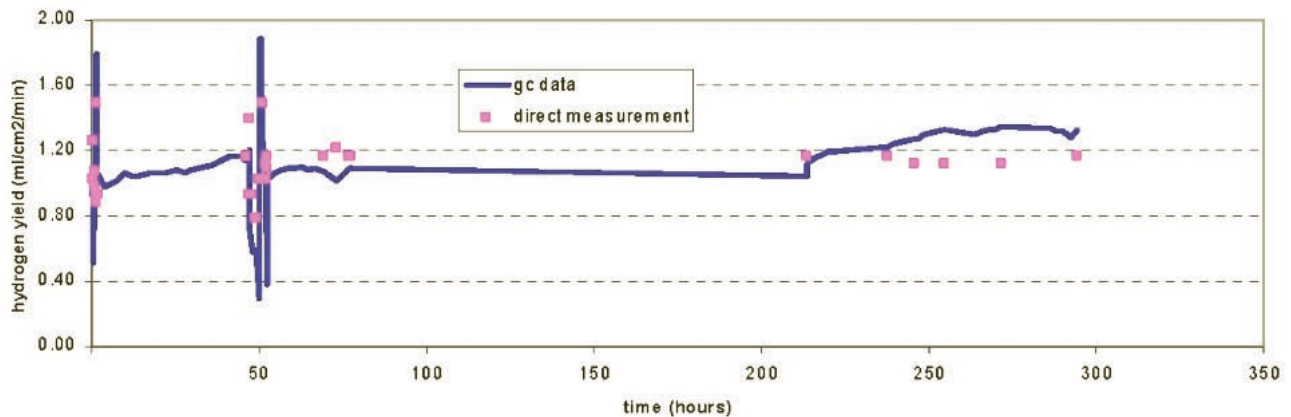


FIGURE 2. Hydrogen Yield Obtained From a Fuel Gas Mixture Containing 200 ppmv H₂S

temperature was raised to 1,050°C at which temperature the yield came close to 2 ml/cm²/min.

Sulfur Tolerance

Lanthanum strontium vanadate (LSV) layers were inked and sintered onto Ni/yttria-stabilized zirconia (YSZ) anodes on electrolyte supported cells. Results from testing on cells in the presence of H₂S are shown in Figures 3 and 4 and the results are even better than what was seen last year with respect to sulfur tolerance. In both cases, a cell without an LSV top layer (screen printed on the anode) was tested for electrochemical

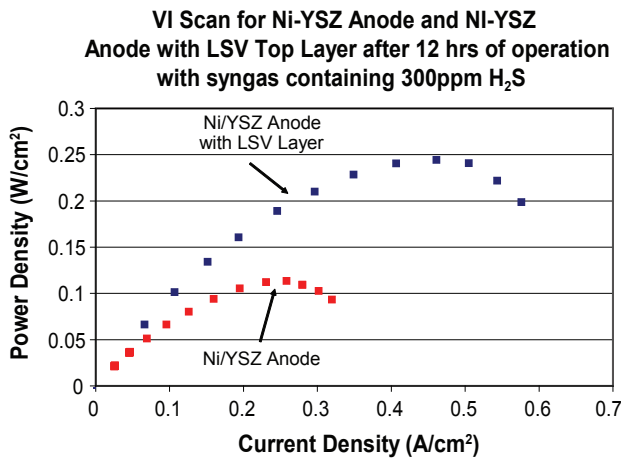


FIGURE 3. Power Density as a Function of Current Density for Ni/YSZ anodes With and Without LSV Layers Exposed to 300 ppm H₂S for 12 Hours

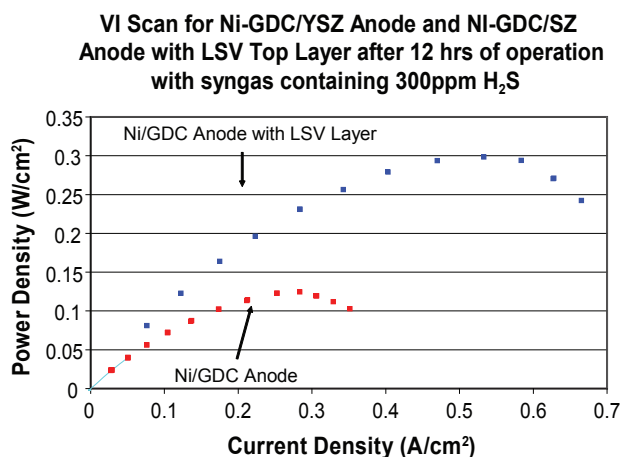


FIGURE 4. Power Density as a Function of Current Density for Ni/GDC Anodes with And Without LSV Layers Exposed to 300 ppm H₂S for 12 hours

power performance. In Figure 3 (red data), the power density of the Ni-YSZ anode is plotted as a function of current density, taken from the voltage-current (V-I) scan of the cell at the 12-hour mark. As can be seen, there is considerable power loss compared to the Ni/YSZ anode with the LSV outer layer screen printed on to the anode surface. These tests were run at a cell temperature of 800°C using the syngas specifications detailed in the project proposal.

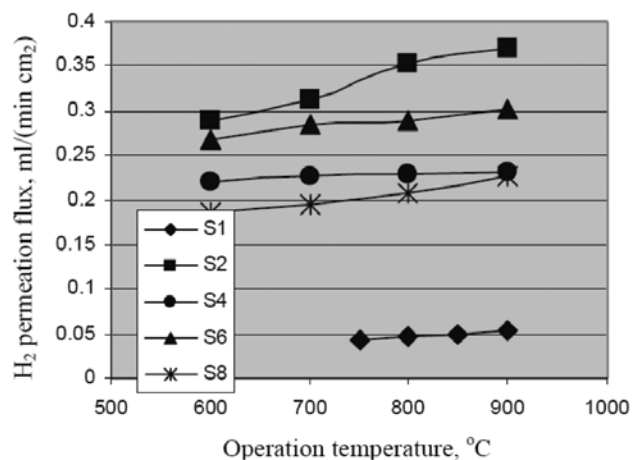
While the initial cell performance is not shown, peak power density attained with an H₂/N₂ blend was 370 mW/cm². This is important to note, because the anode with the LSV outer layer attained a peak power density of 250 mW/cm². This is also important to note because the average power density improvement versus the results from last year is very significant. The power not only increased about 20%, but it improved in the presence of significantly more H₂S. The testing done in the prior year was with 160 ppm H₂S after only six hours of exposure. The testing and results this quarter are for 300 ppm H₂S after twelve hours of exposure.

Ceramic Membrane Separation of Hydrogen

Five compositions were prepared by using ethylenediamine tetraacetic acid (EDTA)-citric acid combined complex method. (SrCe_{0.95}Yb_{0.05}O_{3-δ} [S1], SrCe_{0.90}Yb_{0.05}Tm_{0.05}O_{3-δ} [S2], SrCe_{0.85}Yb_{0.05}Tm_{0.05}Zr_{0.05}O_{3-δ} [S4], SrCe_{0.75}Yb_{0.05}Tm_{0.05}Zr_{0.15}O_{3-δ} [S6], and SrCe_{0.65}Yb_{0.05}Tm_{0.05}Zr_{0.25}O_{3-δ} [S8].) Briefly, the necessary amounts of citric, EDTA acid and NH₃·H₂O were mixed together to form a transparent solution. Then the calculated amounts of Sr(NO₃)₂, Ce(NO₃)₄, Yb(NO₃)₃, Tm(NO₃)₃, and ZrO(NO₃)₂ were added to the citric-EDTA-NH₃·H₂O solution under heating and stirring. The gel was then heated at 120-150°C for several hours to make primary powders, which was calcined at 900°C for 5 hours. The resulted powders were pressed into disks and sintering at 1,500°C for 24 hours. The hydrogen permeation flux for these five pellets was measured under the gradient of H₂+Ar/N₂+O₂. The results are shown in Figure 5. The results indicate that the hydrogen permeation is acceptable, but that the optimal mix of electrical conductivity and hydrogen permeation is yet to be found.

Conclusions and Future Directions

- MEIC membranes can produce a relatively high flux of hydrogen from syngas, but the cost of the production is currently greater than commercial threshold will allow.
- LSV added to gadolinium-doped ceria anodes can be used to significantly increase the sulfur tolerance of solid oxide fuel cells with lower hydrogen content in the fuel gas.



- Ceramic membranes have the potential to provide hydrogen separation in hot syngas but sulfur resistance remains a serious concern.

FY 2007 Publications/Presentations

1. Cooper, M., and Bayless, D.J., Electrochemical H₂S Scrubbing of a Coal Syngas Fuel Stream via SOFCs, *Fifth International Conference on Fuel Cell Science, Engineering and Technology*, Paper FuelCell2007-25042, New York, June 2007.

FIGURE 5. Hydrogen Permeation Flux of These Five Samples