On-Board Vehicle, Cost Effective Hydrogen Enhancement Technology for Transportation PEM Fuel Cells

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Objectives

Develop technology based on an integrated water gas shift (WGS) reactor/Pd membrane H_2 separator for a fuel processor that is capable of producing on-board high purity hydrogen for 50 kWe gasoline-based proton exchange membrane (PEM) fuel cell transportation power plants. This fuel processor design should satisfy DOE's 2005 technical targets for system efficiency, volume, weight, cost, life, start-up time, transient response time and emissions.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- I. Fuel Processor Startup/Transient Operation
- N. Cost

Approach

- Develop a WGS/H_2 separator reactor design integrated into a 50 KWe gasoline-based fuel processing system (FPS) and assess FPS and overall PEM fuel cell (FC) system performance using proprietary, physics-based, validated reactor mathematical models and system level mathematical models.
- Perform trade studies between differential operating pressure, inlet temperature, number of tubes, tube diameter, length and Pd effective layer thickness for the Pd membrane modules to identify optimum reactor design and operating conditions for maximum H_2 recovery efficiency and minimum reactor size/cost.
- Use the models to analyze different reactor and system designs and integration schemes to identify best system efficiency and minimum size/cost.
- Synthesize and assess performance (H_2 permeance, selectivity) of advanced, thin, low cost, long-life, Pd-based, supported (on porous metal supports) membranes.
- Test best Pd membranes under WGS conditions and assess their performance as a function of operating time and number of start up/shut down events (future task).

Accomplishments

- Identified, through reactor models, optimum WGS reactor configuration and operating conditions. H_2 recovery efficiencies up to 96% demonstrated for a membrane reactor operating pressure not higher than 6 atm. Identified best FPS design and Pd membrane reactor integration scheme.
- Demonstrated, through system level models, that a PEM FC power plant with a Pd membrane-based FPS could achieve ~6 points higher efficiency than the conventional system that does not employ a Pd membrane WGS reactor.
- Demonstrated, through system level models, that the FC power plant is in water balance with a ~20% smaller size Energy Recovery Device (ERD) and ~10% smaller radiator and accumulator sizes relative to the baseline power plant.
- Estimated an FPS volume of 1140 W/L, weight of 1100 W/kg, start-up time of <1 minute for 50% of full rated power, transient response time of ~5 seconds and cost of $16/kWe+0.4x (Cost of Baseline FPS).
- Synthesized, by electroless plating and appropriate surface treatment conditions, a ~15 micron, "defect-free" Pd membrane over a porous metal support with H_2 permeance of ~15 m^3/m^2-hr-$atm^{0.5}$ and H_2/N_2 selectivity of 1,100 at 350^{o}C. No membrane performance deterioration was observed in 250 hours of testing and under 10 thermal cycles. Identified the critical characteristics of the porous metal supports for robust and thinner (< 5 microns) Pd membranes.

Future Directions

- Assess capability for Pd deposition on the internal tube surface by electroless plating.
- Obtain porous metal supports with narrower pore size distribution and lower surface roughness on the surface where the Pd phase will be deposited.
- Down select Pd membrane manufacturing process from the critical evaluation of two candidates (electroless plating and UTRC proprietary process).
- Synthesize and characterize low thickness (<5 microns), "defect-free", Pd-Ag alloy membranes with H_2 permeance and selectivity targets of 30-45 m^3/m^2-hr-$atm^{0.5}$ and 2,000 at 350^{o}C, respectively by optimizing porous metal supports.
- Evaluate membrane performance (H_2 permeance and selectivity) and percent H_2 recovery under first stage WGS reformate test conditions.
- Evaluate best membrane performance under an aggressive number of thermal cycling tests (~100 cycles).
- Develop mathematical models from lab-scale tests that predict performance of the reactor under specified life (4,000 hrs for automotive) and start up/shut down events (1,000 for automotive) targets.
- Design, build and test an integrated WGS Pd membrane reactor hardware prototype.

Results

Figure 1 highlights the significant fuel processing system (FPS) simplification that can be achieved with an integrated WGS Pd membrane reactor by comparing this system (Figure 1b) to the conventional one (Figure 1a). Figure 2 (plots (A) through (C)) illustrates some of the trade studies performed to access the optimum WGS Pd membrane reactor operating conditions. H_2 concentration profiles were generated as a function of the reactor length in the high pressure tube side (where the WGS catalyst is located) and in the ambient pressure shell side (where the separated H_2 product and the steam sweep gas flows) to access the changes of the differential H_2 partial pressure

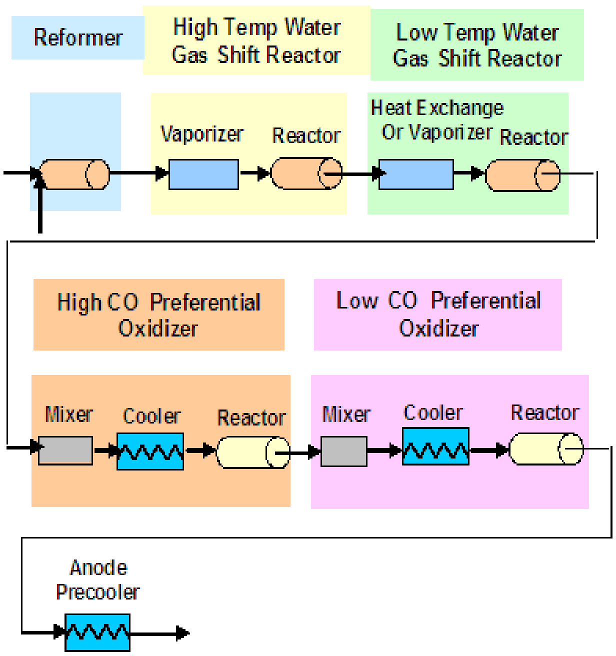

Figure 1A. Schematic of a Conventional Fuel Processing System

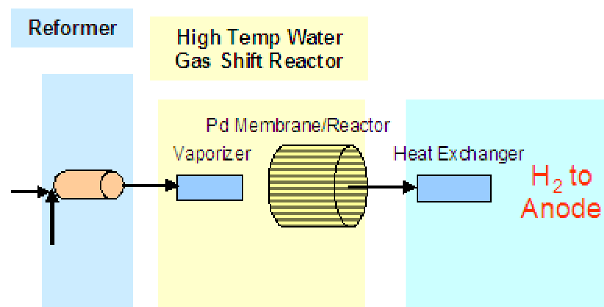

Figure 1B. Schematic of a Pd Membrane-Based Fuel Processing System

(process driving force). It was determined that the amount of WGS catalyst does not account for more than one third of the required reactor volume, while the reactor volume and H_2 separation efficiency depend on the differential operating pressure, membrane thickness, and number and length of membrane tubes. A multi-criteria type of optimization approach was applied to identify the optimum FC system efficiency for a specified operating inlet pressure in the membrane reactor (6 atm). For this system that employs a compressor/expander in order to improve system mechanical efficiency and reduce parasitic power, it was found that with a 7 liter membrane reactor, ~31% FC system efficiency is possible with a ~67% FPS efficiency. The membrane reactor was operated at 85% H_2 recovery efficiency. The results of this simulation are summarized in Figure 3 and imply that a maximum FC power plant efficiency does not necessarily imply a maximum FPS efficiency. However, we recommend this design, since the overall FC system efficiency rather than the FPS efficiency should be maximized. The effective Pd thickness for the Pd membrane reactor that was used in this simulation was ~4 microns, resulting in a H_2 permeance of ~45 $m^3/m^2\text{-hr-atm}^{0.5}$ at 350°C.

Table 1. FPS System Characteristics

Metric	DOE Target	Conventional System	Pd Membrane System
FPS Efficiency	78%	67%	67%*
FPS Power Density (W/L)	> 700	570	1140
FPS Power Density (W/kg)	> 700	550	1100
FPS Cost ($/kWe)	25	C	0.4xC+16
FPS Start Up Time (min)	< 1 min for 33% Full Power (FP)	~3 min for < 50% FP (non optimized)	< 1 min for 50% FP
FPS 10%-90% Transient Response Time	> 5 sec	N/A	~5 sec
PEM FC System Efficiency	N/A	~25%	30.80%

* 77.7% FPS Efficiency can be achieved, but with lower overall PEM FC efficiency

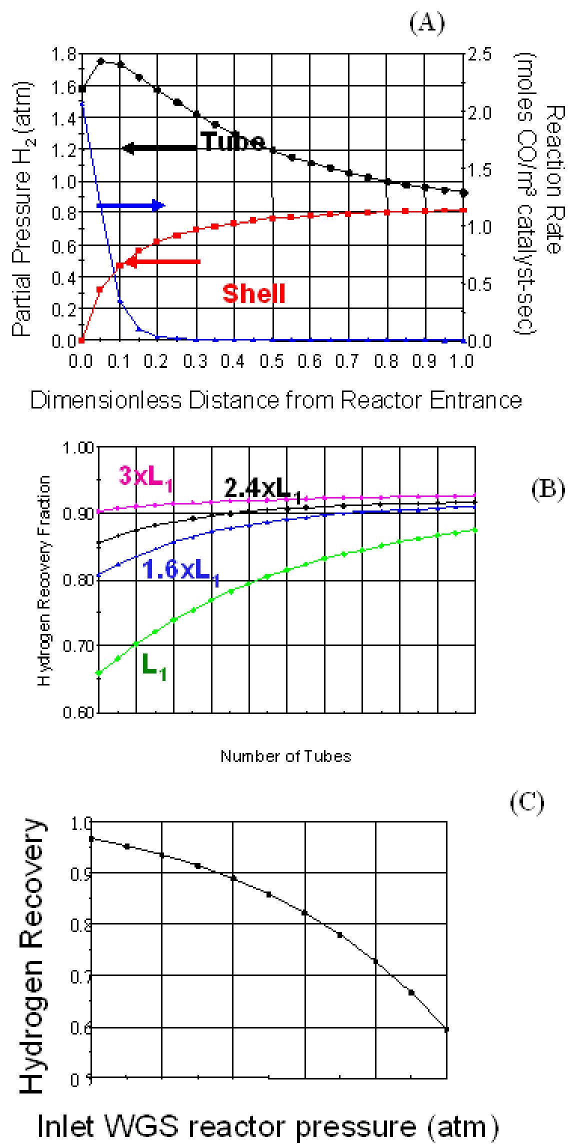

Figure 2. Impact of Operating and Physical Parameters on Performance of the WGS Pd Membrane Reactor

The simulation results for system start-up, shown in Figure 4, illustrate a less than one minute start up time for the FPS for 50% of the full rated power and <5 sec transient response time. This achievement is significant and is due to the elimination of a large number of components from the FPS. In addition, the FPS provides the cells stack with ~100% purity H_2 right from the start. The estimated FPS performance characteristics in comparison to DOE targets are shown in Table 1. As this table illustrates,

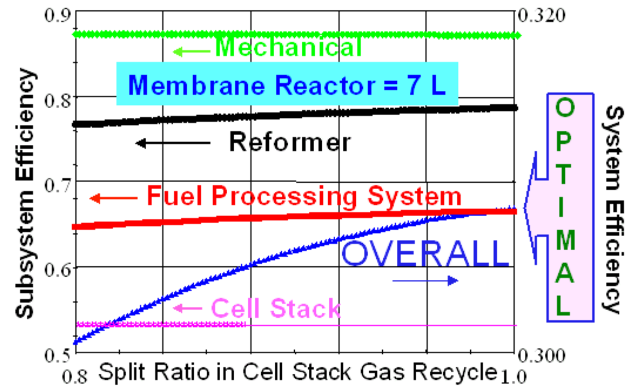

Figure 3. Subsystem and Overall PEM FC System Efficiencies

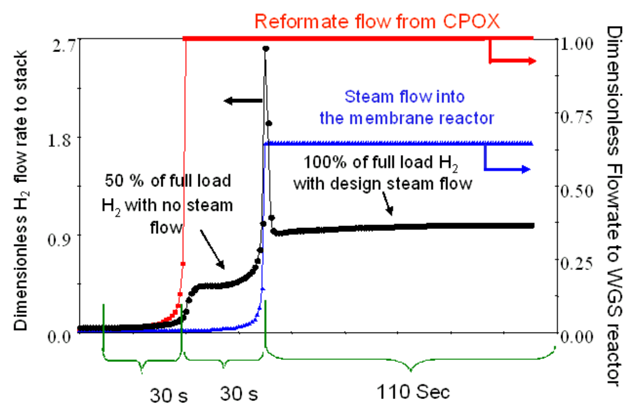

Figure 4. Model Simulation Shows that the Pd Membrane-Based FPS Achieves 50% Power within ~30 Seconds (CPOX = catalytic partial oxidation)

the proposed system design promises excellent progress towards the desirable system targets.

Conclusions

- The FPS design incorporating an integrated WGS Pd membrane reactor satisfies DOE's efficiency, size, start up and transient response targets. Furthermore, the predicted FC power plant efficiency is ~6 points higher than the current system design.
- This design will reduce balance-of-plant volume and cost (ERD, radiator, accumulator), while the significantly simplified system will be easier to control under transients.

- Surface treatment approaches and required support characteristics have been identified that will yield high performance membranes.

FY 2003 Publications/Presentations

1. Mallika Gummalla, Benoît Olsommer, Nikunj Gupta, and Zissis Dardas. "Physics-Based Simulations of Water Gas Shift Membrane Reactor for Prediction Reactor Volume and Performance", Presentation, Abstract, and Presentation Record, American Institute of Chemical Engineers, 2003 Spring Meeting, Fuel Processing Session II, New Orleans, LA, March 2003