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United Technologies Research Center
411 Silver Lane
East Hartford, CT 06108

Technical Point of Contact:

Thomas H. Vanderspurt
Fellow
(860) 610-7172
FAX: (860) 610-7253
vanderth@utrc.utc.com

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

Thomas Vanderspurt (Primary Contact), Zissis Dardas, Ying She, Mallika Gummalla, Benoit Olsommer
United Technologies Research Center
East Hartford, CT, 06108
(860) 610-7172, fax: (60) 610-2453, e-mail: VanderTR@utrc.utc.com

DOE Program Manager: Donna Ho
(202) 586-8000, fax: (202) 586-1637, e-mail: Donna.Ho@ee.doe.gov

ANL Technical Advisor: Thomas Benjamin
(630) 252-1632, fax: (630) 252-4176, e-mail: Benjamin@cmt.anl.gov

Subcontractors:
UTC Fuel Cells, South Windsor, Connecticut
HydrogenSource, South Windsor, Connecticut

Executive Summary

The objective of this effort was to technologically enable a compact, fast start-up integrated Water Gas Shift-Pd membrane reactor for integration into an On Board Fuel Processing System (FPS) for an automotive 50 kWe PEM Fuel Cell (PEM FC). Our approach was to: 1) use physics based reactor and system level models to optimize the design through trade studies of the various system design and operating parameters; and 2) synthesize, characterize and assess the performance of advanced high flux, high selectivity, Pd alloy membranes on porous stainless steel tubes for mechanical strength and robustness. In parallel and not part of this program we were simultaneously developing air tolerant, high volumetric activity, thermally stable Water Gas Shift catalysts for the WGS/membrane reactor.

We identified through our models the optimum WGS/membrane reactor configuration, and best Pd membrane/FPS and PEM FC integration scheme. Such a PEM FC power plant was shown through the models to offer 6% higher efficiency than a system without the integrated membrane reactor. The estimated FPS response time was < 1 minute to 50% power on start-up, 5 sec transient response time, 1140 W/L power density and 1100 W/kg specific power with an estimated production cost of \$35/kW. Such an FPS system would have a Catalytic Partial Oxidation System (CPO) rather than the slower starting Auto-Thermal Reformer (ATR). We found that at optimum WGS reactor configuration that H₂ recovery efficiencies of 95% could be achieved at 6 atm WGS pressure. However optimum overall fuel to net electrical efficiency (~31%) is highest at lower fuel processor efficiency (67%) with 85% H₂ recovery because less parasitic power is needed. The H₂ permeance of ~45 m³/m²-hr-atm^{0.5} at 350°C was assumed in these simulations. In the laboratory we achieved a H₂ permeance of 50 m³/(m²-hr-atm^{0.5}) with a H₂/N₂ selectivity of 110 at 350°C with pure Pd. We also demonstrated that we could produce Pd-Ag membranes. Such alloy membranes are necessary because they aren't prone to the Pd-hydride α-β phase transition that is known to cause membrane failure in cyclic operation. When funding was terminated we were on track to demonstrate Pd-Ag alloy deposition on a nano-porous (~80 nm) oxide layer supported on porous stainless steel tubing using a process designed for scale-up.

Project Summary

Objectives

Develop technology for an integrated Water Gas Shift (WGS) reactor/Pd membrane H₂ separator that is capable of producing high purity hydrogen from an on board gasoline fuel processor for PEM fuel cell transportation power plants. This fuel processor design should satisfy DOE's 2005 technical target requirements for system efficiency, volume, weight, cost, life, start-up time, transient response time and emissions.

Approach

- Develop a WGS/H₂ 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 reactor and system level models.
- Perform trade studies between differential operating pressure, inlet temperature, sweep gas flow rate, number of tubes, tube diameter, length and Pd effective layer thickness for the Pd membrane modules in the WGS reactor to identify optimum reactor design and operating conditions for maximum H₂ recovery efficiency and minimum reactor size/cost.
- Use the models to analyze different reactor and system designs and integration schemes in order to identify best FC system efficiency and minimize FPS size and cost.
- Identify best manufacturing process for thin Pd membranes, scalable for mass production.
- Synthesize, characterize and assess performance (H₂ permeance, selectivity, durability) of advanced, low thickness (< 15 microns), high flux (> 20 m³ H₂/m²-hr-atm^{0.5}) and high selectivity (> 100:1) Pd membranes, supported on tubular porous stainless steel (PSS) supports.

Accomplishments

- Identified, through reactor models, optimum WGS reactor configuration and operating conditions. H₂ recovery efficiencies up to 95% demonstrated for a membrane reactor with an operating inlet 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, beneficial results for the FC water management system.
- Estimated an FPS volume, weight, cost, start-up time and transient response time equal to 1140 W/L, 1100 W/kg, \$35/kW, < 1 minute for 50% of full rated power and 5 sec, respectively.
- Electroless plating was found to be the best manufacturing process for the synthesis of thin and durable supported Pd membranes on tubular PSS supports.
- Identified porous tubular supports with narrower pore size distribution and lower surface roughness coated with a ceramic layer in order to eliminate the intermetallic diffusion problem during membrane operation at elevated temperatures.
- Synthesized, by a modified electroless plating process, a "defect-free" Pd membrane over porous stainless steel tubes with a world-class H₂ permeance of ~50 m³/m²-hr-atm^{0.5} and H₂/N₂ selectivity of 110:1 at 350 °C. No membrane performance deterioration was observed during 280 hrs of testing and under 10 thermal cycles.
- Demonstrated the synthesis of a Pd-Ag alloy membrane.

Final Report Body

Introduction

The goal of this project is to develop technology for an integrated Water Gas Shift (WGS) reactor/Pd membrane H_2 separator that is capable of producing high purity hydrogen from an on board gasoline fuel processor for PEM fuel cell transportation power plants. This fuel processor design should satisfy DOE's 2005 technical target requirements for system efficiency, volume, weight, cost, life, start-up time, transient response time and emissions.

This disruptive technology is the only way to reduce the size, cost and start up time of the fuel processor since it eliminates a substantial number of components. More specifically, in addition to shifting the Water Gas Shift equilibrium towards higher H_2 production, it reduces the number of reactors after the gasoline desulfurizer from 5 to 2 while it eliminates a total of 7 components downstream of the reformer from the current FPS design. Additional benefits to the FC power plant also arise due to the fact that it supplies "pure" H_2 instead of reformat to the PEM cell stack: The same power output can be achieved with a ~30% smaller cell stack, resulting in significant cost benefits while it avoids the gradual CO poisoning effect of the cell stack. Finally, water management in the cell stack, currently a critical issue driven by the high flow rate of the diluted in hydrogen reformat, will be significantly improved, since the flow rate in the anode will be reduced.

Results

Modeling Analysis: Reactor and System

Figure 1 highlights the significant fuel processing system (FPS) simplification that can be achieved with an integrated WGS Pd membrane reduction by comparing this system (Proposed System) to the conventional (Baseline System). It also illustrates the favorable shift in the WGS thermodynamic equilibrium towards more high production at elevated temperatures due to the continuous removal of the hydrogen product from the reaction zone. At the component level, a detailed Pd Membrane/WGS reactor model has been developed with steam as sweep gas. The reactor configuration consists of an array of Pd membrane tubes, filled with the WGS

catalyst extrudates, as shown in Figure 2, operated at elevated pressure while the sweep gas flows in the reactor shell. The sweep gas dilutes the H_2 product and reduces the H_2 partial pressure, thus increasing the separation process driving force. The steam sweep gas is generated primarily by cooling the membrane effluent gas stream from ~ 450 °C to the PEM fuel cell inlet temperature (83 °C) and the exhaust from the fuel cell system. Modeling results showed that a membrane reactor efficiency as high as 95 % can be reached if adequate membrane surface area is provided and the long-term H_2 permeance membrane target is achieved by the membranes development effort.

Figure 1. The FPS system simplification due to the Pd membrane WGS reactor and the favorable shift of the WGS equilibrium.

Figure 2. Schematic of an integrated WGS Pd membrane reactor.

Figure 3, plots (A) through (C), illustrate some of the trade studies performed to determine the optimum WGS Pd membrane reactor operating conditions. H_2 concentration profiles were generated as a function of the reactor length in the higher pressure, catalyst side and in the H_2 /steam sweep gas side to assess the changes of the differential H_2 partial pressure (process driving force). The high activity catalyst

accounted for about one third of the required reactor volume while the reactor volume and H_2 separation efficiency depend on the differential operating pressure, membrane thickness, number and length of membrane tubes.

PlotB

Plot C

Figure 3. H_2 concentration profiles as a function of the distance from the reactor inlet, A; number of membrane tubes for different tube lengths, B; and inlet WGS pressure, C.

A multi-criteria optimization approach to identify the optimum FC system efficiency was used. For

a 6 atm inlet pressure, 7 L membrane reactor recovering 85% of the H_2 the optimum PEM FC system efficiency was 31% at 67% FPS efficiency. This design for a UTC FC ambient pressure PEM FC power plant used a compressor/expander to improve mechanical efficiency and reduce parasitic power requirements. For faster start-up and transient response as well as lighter weight and smaller volume this FPS employs a Catalytic Partial Oxidizer (CPO) and not an Autothermal Reformer (ATR). An ATR would require an on-board steam generator. The CPO does reduce system efficiency by about 4 %. The results of this simulation show that a maximum FC power plant efficiency does not necessarily imply a maximum FPS efficiency. To achieve this performance a H_2 permeance of $\sim 45 \text{ m}^3/\text{m}^2\cdot\text{hr}\cdot\text{atm}^{0.5}$ at 350°C was assumed. Therefore, this was the project H_2 permeance target for the Pd membrane development effort.

Our modeling shows that the integrated CPO WGS/Pd membrane FPS system can produce $\sim 50\%$ of its full potential H_2 in less than 1 minute, Figure 4. To provide the cell stack with pure H_2 at the cell stack temperature the only component downstream of the WGS/membrane reactor is a heat exchanger that generates steam by cooling the H_2 . 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 $\sim 100\%$ purity H_2 right from the start.

Figure 4. Simulation results of a start up of an FPS with a Pd membrane WGS reactor.

Simulation results also have shown (see Figure 5) that a 7 L membrane reactor for a 50 kW gasoline power plant (in a configuration that yields the best fuel cell system efficiency of $\sim 30.8\%$), has a 4 second response time for a down transient from 90 to 10 % power and 7

seconds for an up transient from 10 to 90 % power. An implicit assumption of a flow control time of 1 second was made. This transient response meets the project technical goals.

Figure 5. Simulation results for a 90% to 10% down transient for the Pd membrane reactor.

System level models demonstrated that the FC power plant is in water balance with a ~20% smaller Energy Recovery Device (ERD) and ~10% smaller radiator and accumulator compared to the baseline power plant.

Table 1 shows the estimated FPS performance characteristics in comparison to DOE targets and illustrates the excellent progress the proposed system design makes towards those targets. Specifically the estimated cost of this fuel processor, assuming a 6 μm thick pure Pd equivalent membrane in the WGS reactor, is equal to 40% of the cost of the Conventional FPS, shown in Figure 1a.

Table 1. FPS system characteristics.

Metric	Target	Status
SYSTEM SPECIFIC		
FPS Efficiency	78%	78%
FPS Power Density	> 700 W/L	1140 W/L
	> 700 W/Kg	1050 W/Kg
FPS Cost	\$25/kWe	\$ 35/kWe
FPS Start Up Time	1 min for 33% Full Power	1 min for 50% Full Power
FPS 10%-90% Transient Time	5 sec	5 sec
CO (ppm)	10 ppm	< 10 ppm expected
MEMBRANE SPECIFIC		
H ₂ Permeance ($\text{m}^3/\text{m}^2\cdot\text{h}\cdot\text{atm}^{0.5}$)	35	50
H ₂ Selectivity for 99.999% H ₂ Purity (Rest: CH ₄ , N ₂ , CO ₂)	100-150	120
Durability	> 4,000 hrs	No performance deterioration for 350 hrs

Pd Membrane Synthesis, Characterization and Testing

We have selected porous stainless steel (PSS) tubes as supports for the Pd membrane development effort. The main advantages of porous stainless steel (PSS) supports over porous ceramics, Vycor glass, Ta, V and other configurations such as palladium foils are the resistance to cracking and the simplicity of module construction. It was also found that the surface roughness and the pore size distribution on the surface of the PSS play a critical role towards the development of thin, “defect-free” Pd membranes. For that reason, PSS substrates with ~3 times smoother external surface vs. the commercially available 0.1 microns were developed by a commercial supplier. In addition, tubular PSS substrates coated with a ceramic layer, whose pore size ranges from 0.02 to 0.1 μm , were identified. These substrates allowed the synthesis of thinner Pd membranes with capability to operate at temperatures higher than 450°C. The former was due to the expected lower surface roughness of the support while the latter due to the fact that the ceramic layer provides a barrier to the intermetallic diffusion of the metal support into the Pd phase.

The electroless plating (EP) was selected for the synthesis of the supported Pd membranes. This process can effectively handle any type of support geometry and can be easily scaled up for mass production. It also results in minimal waste since the solution with the excess Pd can be reused and it provides the highest Pd phase hardness and the strongest bonding to the porous support relative to other synthesis processes that were investigated (electroplating and physical vapor composition). The only disadvantage is that it is quite elaborate, consisted of multiple steps (support activation and Pd deposition) but we have made progress in that area by reducing the number of required steps by ~50%.

The electroless plating process consists of pre-treatment of the porous metal support, in-situ formation of an oxide layer to minimize the intermetallic diffusion for long term membrane stability, if the PSS supports are not coated with a thin ceramic layer, surface activation and sequential plating of Pd followed by high temperature calcinations. The surface activation procedure consists of successive immersions in an acidic SnCl_2 bath (sensitizing) followed by an acidic PdCl_2 bath. After immersion in the SnCl_2 bath, the PSS support is rinsed gently with

deionized water. Rinsing with 0.01 M HCl and then with water is carried out after immersion in the PdCl_2 bath. The 0.01 M HCl solution is used to prevent hydrolysis of Pd^{2+} ions. Palladium deposition occurs according to the following auto-catalytic reaction:

The activation stage reduces the induction period at the beginning by depositing Pd nuclei. A typical plating bath contains a plating agent (e.g., palladium tetra-amine chloride, $\text{Pd}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$), stabilizing agent (e.g., EDTA salt) and reducing agent (e.g., hydrazine). The thickness of the Pd layer is estimated by the washed membrane weight gain or can be determined directly from a SEM picture (a destructive method since it requires dissection of the membrane module).

Outstanding tubular Pd membranes have been demonstrated as a result of a proprietary modification of the previously described electroless plating process. More specifically, a H_2 permeance of $50 \text{ m}^3/(\text{m}^2\text{-hr-atm}^{0.5})$ with a H_2/N_2 selectivity of 110 at 350°C was achieved as shown in Figure 6. No membrane performance deterioration was observed during the 280 hrs of testing and under 10 thermal cycles. The achieved permeance exceeded the project goal of $45 \text{ m}^3/(\text{m}^2\text{-hr-atm}^{0.5})$, it was reproducible and was higher than any known literature value.

Figure 6. Permeance and selectivity of synthesized Pd membranes.

We have strong evidence that this high H_2 permeance was due to the unusual morphology of the Pd layer as a result of the proprietary modifications to the process mentioned earlier. Micrographic examination of the interface between the palladium layer and PSS substrate revealed that there is a good bond between palladium layer and the stainless steel substrate. The observed palladium thickness Figure 7B. is in a good agreement with that calculated from experimental data.

Figure 7. Microstructure of Pd layer deposited by conventional electroless plating (EP) process (top figure) and a modified by UTRC EP process (bottom figure). Both layers had about the same nominal thickness.

Alloy elements play an important role in overcoming the potential problem of Pd embrittlement during the power plant shut down. As a function of temperature and hydrogen partial pressure Pd-hydrogen interactions give rise to a β -phase, unstable above 310°C and an α -phase, stable at high temperatures and characterized by a markedly lower hydrogen content. The α - β transformation, occurring for pure Pd near room temperature, causes serious alteration in the atom spacing of the metal

lattice. The consequent dimensional changes could distort the membrane, making it less mechanically resistant and more brittle and prone to rupture. As a result, the resistance to repeated start-up/shut down cyclic stresses could be low. Fortunately, elements such as Ag, Ru and Rh stabilize the α -phase against the β -phase, reducing the problem of embrittlement. More specifically, 30 wt. % of Ag stabilizes the α -phase even at room temperature. The equilibrium adsorption of hydrogen in the Pd-Ag alloy increased as the relative amount of silver in the alloy increased. However, the diffusion coefficient of hydrogen in the alloy decreased with increasing silver content. Since the permeability is the product of the solubility coefficient and diffusion coefficient, as a result of these two opposing factors, the hydrogen permeability for a Pd-Ag alloy has its maximum value at 23 wt% Ag content.

Synthesis of a Pd-Ag alloy that should be more permeable to hydrogen and also more resistant to hydrogen embrittlement was achieved by electroless plating on the surface of 0.1 μm PSS substrate as shown Figure 8. This membrane was synthesized by depositing a Pd layer on the PSS substrate first and subsequently depositing a Ag layer on it. This was more of a challenge, since little work in the literature deals with electroless plating of Ag using hydrazine as the reducing agent. It is known, however, that commonly used complexing agents such as citric acid or EDTA have small complexing ability for Ag, which makes it difficult to stabilize the electroless silver deposition bath. Therefore, the use of dilute silver solutions as the deposition bath is favored. Compared to Pd, silver has a relatively low activity for the electroless plating. Thus, the electroless deposition of Ag needed to be initiated by foreign nuclei, for example, Pd. This is the reason that Ag was deposited after deposition of the thin Pd film on the support is completed. The Pd-Ag alloy was formed by heating (annealing) this material system in an inert atmosphere at 500°C for ~ 6 hours. The existence of the ceramic oxide interlayer also offers the opportunity to increase the heat treatment temperature to 600°C and significantly reduce the dwelling time. Co-deposition of Pd and Ag particles with the electroless plating process has been investigated but was not successful due to the different deposition kinetics of Pd and Ag.

Figure 8. Pd-Ag alloy membrane Electron Micrograph and PXRD pattern confirming alloy formation.

The nominal thickness of the generated 52%Pd-48% Ag alloy membrane layer was ~23 μm and its H_2 permeance was 17.3 $\text{m}^3/(\text{m}^2 \text{ hr atm}^{0.5})$ at 400°C. This is higher than that expected 13 $\text{m}^3/(\text{m}^2 \text{ hr atm}^{0.5})$ for a Pd membrane of the same thickness and demonstrates the benefit of alloy formation. Due to the termination of this contract, the effort to further reduce the membrane thickness and achieve the more desirable 77%Pd-23%Ag alloy composition was stopped.

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 that does not employ an integrated WGS Pd membrane reactor. This design also reduces the BOP volume and cost (ERD, radiator, accumulator) while the significantly simplified system will be easier to control under transients.
- A modified electroless plating process resulted in a world-class tubular Pd membrane with H₂ permeance of 50 m³/(m²-hr-atm^{0.5}) and H₂/N₂ selectivity of 110 at 350°C. This membrane did not show any sign of performance deterioration for the 280 hrs tested and after 10 thermal cycles between 450 °C and 350°C.
- The modified electroless plating process developed by UTRC resulted in a different morphology of the Pd phase, which we believe is responsible for the unusually high permeance relative to the layer thickness. The Pd deposition process has been further optimized by eliminating the number of steps by ~50% and is fully scalable for mass production.

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.
2. Zissis Dardas, Mallika Gummalla, Ying She, Thomas H. Vanderspurt, "Integrated WGS Pd Membrane Reactor for Compact Hydrogen Production Systems from Reforming of Fossil Fuels", Presentation and Abstract, 13th International Congress on Catalysis, Paris, France, July 2004.

3. Mallika Gummalla, Zissis Dardas, Thomas H. Vanderspurt, Ying She, Benoît Olsommer, "System Level Simulations and Analysis of Fuel Cell Power Plant with an Integrated WGS Pd Membrane Reactor", Presentation and Abstract, 13th International Congress on Catalysis, Paris, France, July 2004.