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ABSTRACT

High temperature hydrogen separating membranes have the potential to increase the efficiency of the coal-based electrical/chemical plants of the future. Palladium (Pd) alloys are attractive materials as membranes due to high permeability and relative robustness. A main drawback is the high cost of Pd metal so that thin metal films supported by hydrogen porous substrates are imperative. Pure Pd also suffers from hydrogen embrittlement and poor resistance to thermal cycling. Membrane configurations consisting of thin films (< 20 μm) of Pd alloys on hydrogen-porous substrates will help to alleviate cost and embrittlement problems. The membranes will be employed in the water gas shift reaction to produce purified hydrogen.

INTRODUCTION

The palladium membrane reactor (PMR) is a combined permeator and catalytic reactor (Figure 1). Catalysts are used to foster reactions such as methane steam reforming, $CH_4 + H_2O \rightarrow 3H_2 + CO$, and water-gas shifting, $H_2O + CO \rightarrow H_2 + CO_2$. Due to thermodynamic equilibrium limitations these reactions only proceed to partial completion. Thus, a tubular $PdAg_{23}$ (wt.%) membrane with ~175 μm thick walls, which is exclusively permeable to H_2, was incorporated into the reactor. By maintaining a H_2-partial-pressure gradient across the membrane, H_2 removal through the membrane enabled the reactions to proceed toward the product side.

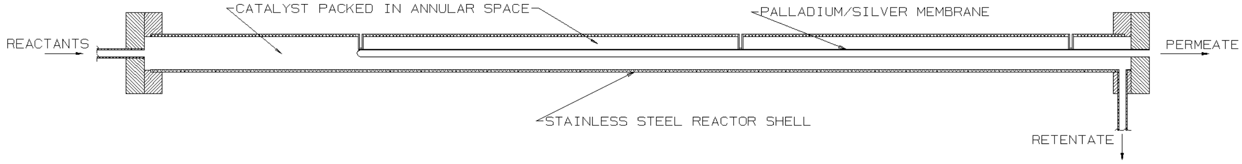

Figure 1. The Palladium Membrane Reactor.

PMR's have significant advantages in efficiency over other fuel processing systems. Several components are usually required in conventional steam reforming systems. For example, a high-temperature reformer, a low-temperature reformer, a high-temperature shifter, and a low-temperature shifter are typically used in methane steam reforming to obtain as much pure H_2 as possible. Heat exchange, gas separation, and air or water injection are required between reactors, resulting in expensive control systems, multiple unit operations, and high energy consumption. In addition, a large quantity of excess water and high operating temperatures (~800°C in the case of methane) are needed to obtain good conversion and prevent coking (carbon deposition on the catalyst). The multiple process steps, excess water requirements, and high operating temperatures of a conventional reformer result in a large and inefficient system. With a PMR system only one reactor is required and it operates at a lower, more efficient temperature than conventional reformers and requires a lower steam/hydrocarbon ratio.

PMR's have been used to convert hydrocarbons into pure H_2[1-7]. This process holds promise for generating H_2 for fuel cell use or for H_2-consuming reactions in the chemical and petrochemical industries. The PMR has been under development at Los Alamos since 1992 (refs. 1-7). During this time, PMR performance has been characterized with respect to inlet conditions (i.e., hydrocarbon-to-water ratio), temperature, pressure, geometry, and catalyst type. This information has been analyzed and incorporated into a mechanistic model for use in design and optimization. The PMR system has run for 215 days of around-the-clock operation over an 18-month period with high performance and reliability. Thus far, simulated coal gas, methane, methanol, ethanol, octane, and gasoline have been reformed in a PMR. Upwards of 99% of all the injected H_2 (in the form of water and hydrocarbons) were converted to pure H_2 for each of the fuels. The retentate (i.e., effluent from the high-pressure side of the reactor) was essentially pure CO_2 for each of the fuels, with the impurities consisting of a small quantity of unreacted fuel, H_2, H_2O, CH_4, and CO.

Although membrane reactors hold the promise of improved fuel processing efficiency, their costs are high due to the use of Pd metal and issues such as hydrogen embrittlement and sulfur tolerance need to be addressed. The $PdAg_{23}$ membranes used in previous experiments were tubes with a wall thickness of 178 μm. This is far too much Pd to be cost effective in an energy application. Development of composite membranes comprised of a thin Pd or Pd alloy film on a hydrogen-porous support or less expensive alternatives to Pd is required. Some advances have recently been made in achieving thinner membranes. For example, a composite membrane with Pd thickness as small as 0.5 μm has been developed.[8] These composite metal membranes have low Pd loadings and high H_2 fluxes (~29 $sccm/cm^2 \cdot atm$ at 365ºC).

A Pd membrane reactor was used to produce pure H_2 and a CO_2 rich stream from carbon monoxide and water over commercially available catalysts.[9] These preliminary results demonstrate the viability of high pressure PMR operation. As much as 87% of the injected CO was converted into H_2 over an Fe-Cr-Cu oxide catalyst at 343°C, a pressure of 240 psia, and a H_2O:CO ratio of 2.6. The PMR has great potential in energy applications since it operates at more efficient conditions than conventional reforming and shifting systems and it produces pure H_2 for use in power generation and CO_2 for carbon sequestration. However, in order for PMRs to become a viable technology for energy applications, sulfur tolerance must be improved, membrane thickness (and therefore cost) must come down, and membrane fluxes and lifetimes must be improved.

Sulfur is ubiquitous in coal and must be removed prior to discharge of coal combustion products to the environment. Whether or not sulfur is removed up front or at the tail end of the overall process, sulfur tolerant membranes and catalysts are desired for systems utilizing coal gas. The $PdCu_{42}$ alloy has been reported to be sulfur tolerant.[10-11] Our work focuses on creating thin film composite membranes using this material.

DISCUSSION OF CURRENT ACTIVITIES

MEMBRANE DESIGN

The Pd membrane literature was reviewed and two of the most promising configurations are being fabricated. A Pd-alloy/refractory/Pd-alloy composite foil membrane (developed at Los Alamos National Lab), and Pd alloy thin films on porous ceramic supports.[8,12] The foil composites are prepared by ion cleaning a refractory metal (V, Nb or Ta) or alloy and sputter depositing Pd (or Pd alloy) onto it *in-situ*. This eliminates the oxide/contaminant layer between the Pd and the foil resulting in higher hydrogen permeability.

The other method of composite membrane fabrication involves wet chemical methods. Commercially available porous ceramic membranes are cleaned, the ends are glazed, the surface is activated, and then they are electroless plated with Pd and then Cu. The membrane is heated in-situ to moderate temperatures (350-550ºC) to promote intermetallic diffusion of the two metals. Characterization of both types of membrane materials is ongoing with respect to permeability and thermal stability under the water-gas shift reaction conditions.

PMR DESIGN

A test module has been designed and is being fabricated to accommodate tubular composite membranes (Figure 2). The catalyst particles are packed within the hydrogen separating membrane and the shell collects the permeated hydrogen. The new PMR test bench (Figure 3), with all stainless steel components will be used to test various catalysts and membrane materials at high pressures (up to 15 atm) for hydrogen recovery during reforming reactions as well as the impact of sulfur on performance.

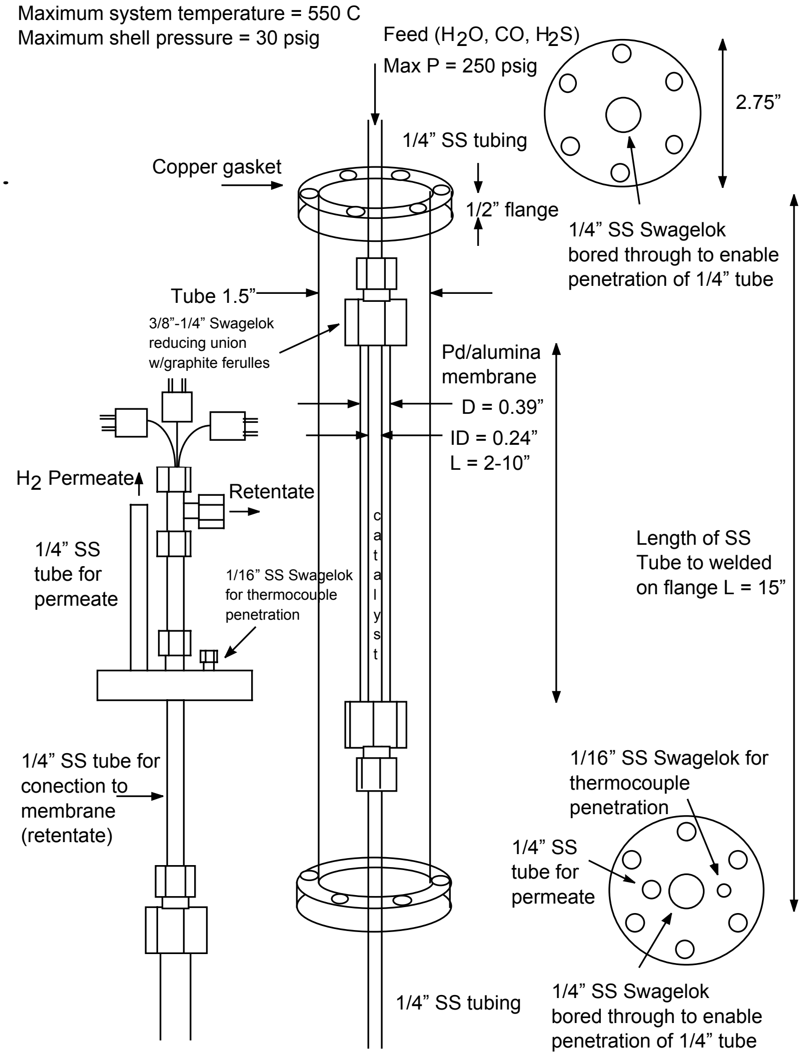

Figure 2. Schematic of composite membrane testing module.

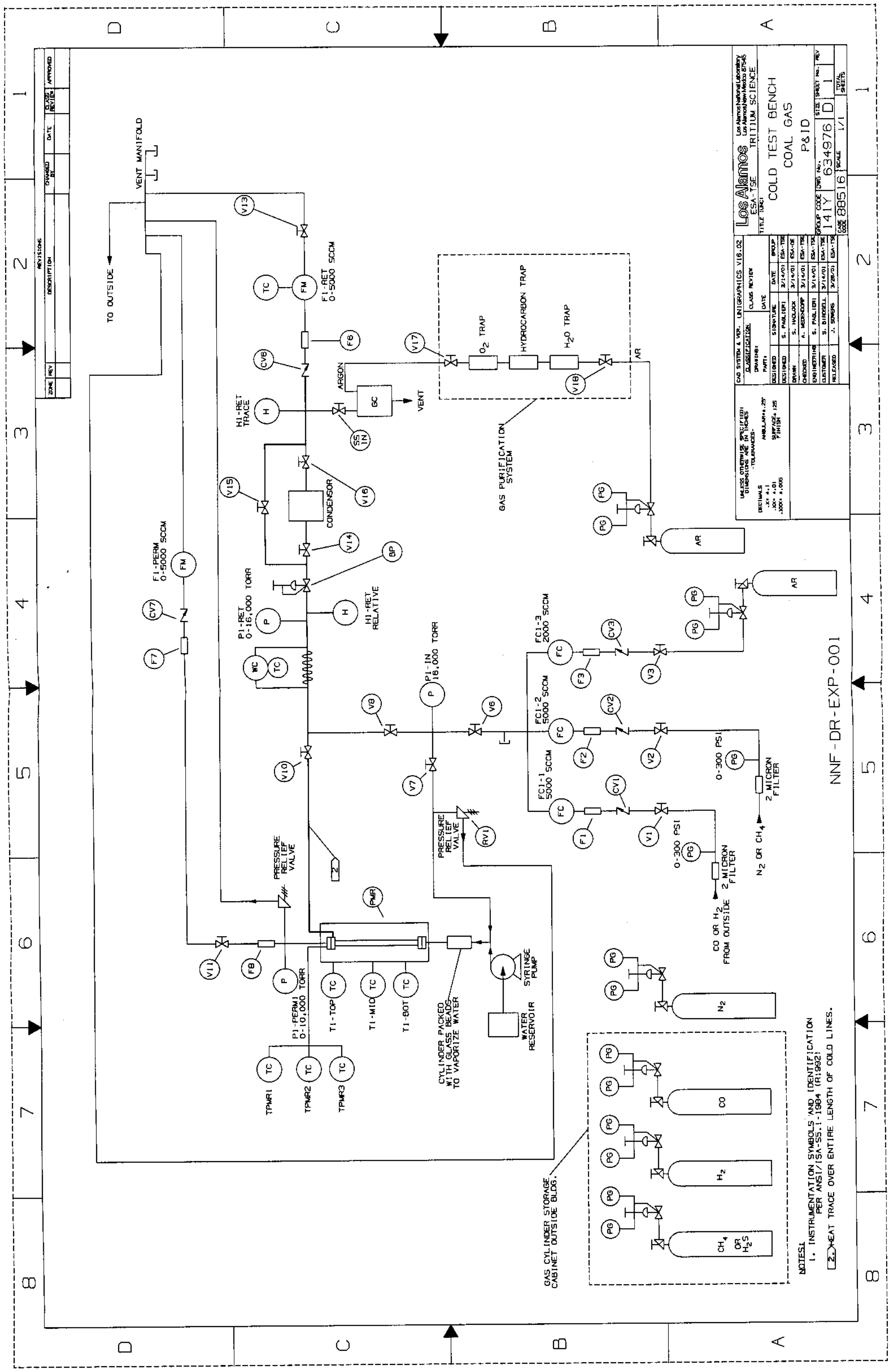

Figure 3. Test bench schematic.

CONCLUSIONS

The use of Pd alloy thin film composites will help lower the cost of hydrogen separation membranes while the use of alloys will reduce hydrogen embrittlement problems and may impart increased sulfur resistance. Fabrication and characterization of these materials for use as membrane reactors to test various catalysts is in progress.

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