(20) Development of a Pilot Scale module for Hydrogen Separation

The key objective of this two-year effort is to advance Research triangle institute's hydrogen separation membrane technology to a pilot scale unit. The proposed effort will optimize membrane synthesis parameters to reduce the cost of the membranes while meeting the hydrogen flux and selectivity targets as well as to make them robust, long-term, durable, and tolerant to impurities including sulfur species typically present in synthesis gas derived from a variety of feedstocks, e.g. natural gas, coal and biomass feedstocks.

Total project cost: $1,000,000
Funding request: $800,000
Project Lead: NYSERDA
Project Participants: North Carolina State Energy Office; Research Triangle Institute; Pall Corporation

Start Date: October 1, 2005
End Date: October 1, 2007

Presentations/Publications

None.

Patents

None.

Progress in Past Quarter and Current Status

During this reporting period evaluation of two sets of AccuSep substrate tubes received from Pall Corporation during the last reporting period was completed. The two sets of AccuSep substrate tubes consisted of six (6) tubes each of two different designs. One set of tubes is approximately 0.41" in diameter and consisted of 9" long porous media with non-porous ¼" OD stainless steel tubes welded to both ends (the tubes designated as NPE). The other set of tubes consisted of approximately 7" long porous media section, 0.46" in diameter tapered to 0.41" OD to allow use of standard 10 mm Swagelok fittings. Since the ends of this set of tubes were porous, these tubes are designated as PE. The support material for NPE tubes was made from 316L porous stainless steel (SS) having a 0.8 micron average pore diameter, whereas, the support material for PE tubes was made from 316L porous stainless steel (SS) having a 2.0 micron average pore diameter. The porous stainless steel sections of all tubes were covered on the outside surface of the tubes by a zirconia layer with a nominal pore size of 0.1 micron. Due to the finer pore size, the integrity of zirconia coating was determined to be better for the NPE tubes as measured by fluid (Pallsol – Pall Corporation's proprietary test liquid) flux rate through the support tubes at a constant fluid pressure differential.

Pd-alloy composite membranes were prepared using tubes from both sets. As noted in the last quarterly report, high hydrogen flux rates were again observed for Pd-alloy composite membranes prepared with each type of the substrate design as shown in Figures 1 and 2 for NPE-6 and PE-5 composite membrane tubes. While successful composite membranes were prepared with these substrate materials as indicated by the above described performances as well as those reported in the last quarterly report, the porous stainless steel support material has been found to be sensitive to the aqueous solutions causing detachment of the ceramic zirconia layer from the porous stainless steel at isolated spots in some of the membrane preparations. Two tubes in each set of the tubes could not be tested for permeation due to isolated peeling areas on the tube surfaces. The problem has been traced to residual ionic solutions left in the porous stainless steel matrix after rinsing the tubes in DI water. Discussions with Pall Corporation confirmed the sensitivity of porous stainless steel to ionic aqueous solutions involved in the aqueous-phase electroless plating process. Thorough rinsing of the membrane tubes with deionized water after every processing step is considered to be the primary remedy and is currently practiced.

Although the composite membranes prepared with the tubes of the two distinct support designs indicated similar hydrogen flux rates the observed pure component hydrogen to nitrogen selectivity was decidedly much greater with NPE type tubes as compared with PE type support tubes. For example, the hydrogen permeation rates shown in Figures 1 and 2 for NPE-6 and PE-5 composite membranes were similar, however, the pure component hydrogen to nitrogen selectivity for NPE-6 membrane at 600 ^{o}C and 40 psi pressure differential was about 2,080 and that for PE-5 composite membrane was about 285 for the same permeation test conditions. The smaller pore size in the porous stainless steel and the improved zircoia coating integrity in NPE tubes are the likely reasons for the observed greater selectivity of the composite membranes prepared with NPE tube supports.

In addition to the underlying porous stainless steel pore size and porosity, the smoothness of the surface of the ceramic zirconia layer is also expected to have an influence on the palladium membrane coating process and the performance of the composite membrane. Pall Corporation has developed a process to prepare zirconia layers with different surface smoothness as measured in micro-inches by a Taylor-Hobson, Tallysurf profilometer. A batch of six substrate tubes was prepared by Pall Corporation with similar stainless steel porous material as in the NPE tubes but with smoother surface with surface roughness in the range of 35 to 45 micro-inches. These tubes will be evaluated next for the composite membrane performance characteristics.

<u>Plans for Next Quarter</u>

During the next quarter additional Pd-alloy composite membranes will be prepared and tested for permeation characteristics in an iterative process of substrate and membrane optimization in Task 1 to meet the hydrogen flux target. Additional substrate tubes will be received from Pall Corporation for preparing composite membranes. Procedures will be established to prevent any possibility of delamination of the ceramic layer at isolated spots observed in some of the membrane preparations. Possibility of obtaining all ceramic substrate media will be investigated by Pall Corporation. Selected composite membrane tubes prepared to date will be analyzed by Pall Corporation by cross-section SEM analysis.

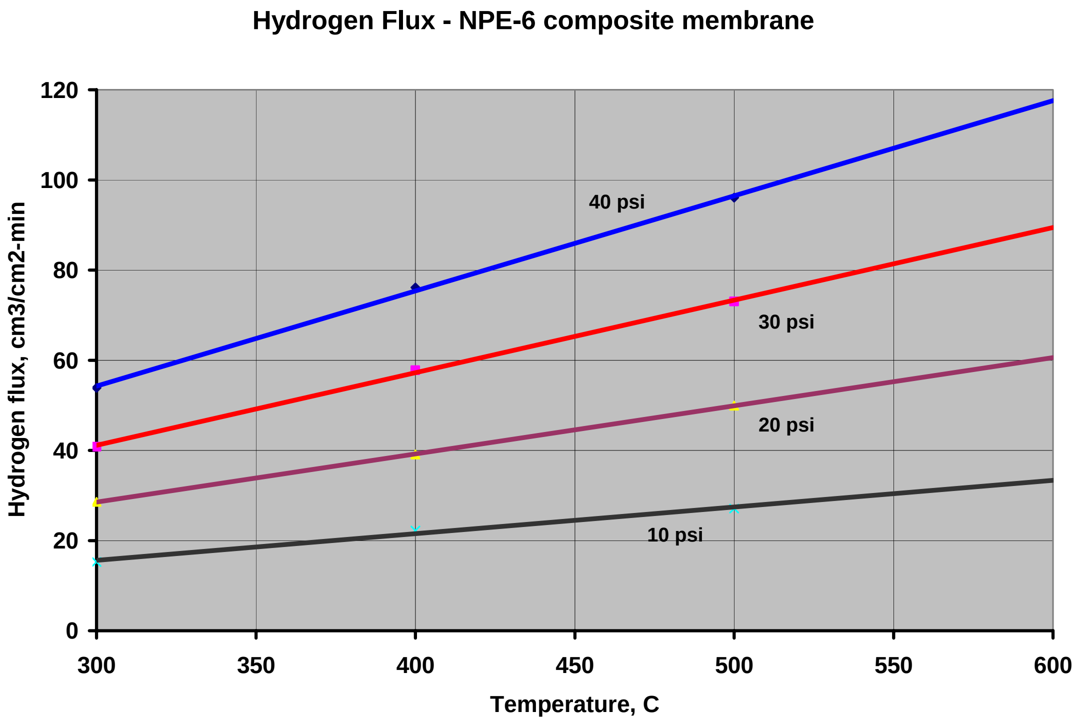

Figure 1. Observed hydrogen permeation rate as a function of temperature and trans-membrane hydrogen partial pressure differential for the NPE-6 composite membrane

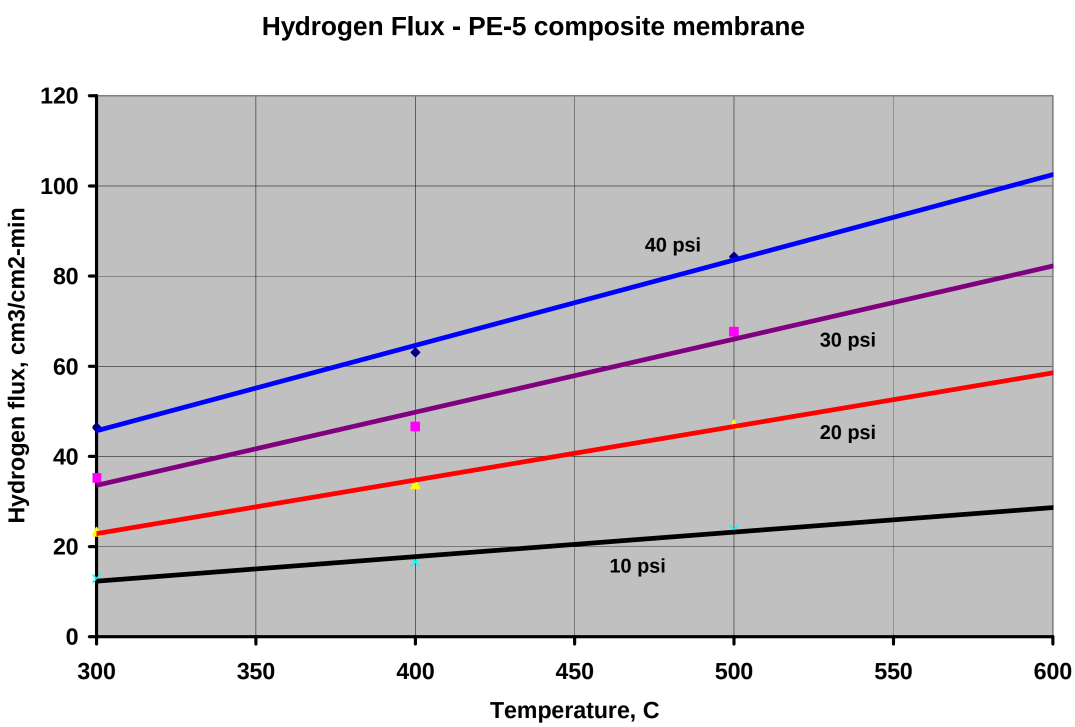

Figure 2. Observed hydrogen permeation rate as a function of temperature and trans-membrane hydrogen partial pressure differential for the PE-5 composite membrane