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**Texas Commission on Environmental Quality**
**New Technology Research & Development (NTRD) Program**
**Monthly Project Status Report**

Contract Number: 582-5-65591-0002 .

Grantee: The University of Texas at Austin .

Date Submitted: December 12, 2005

Report for the **Monthly** period:

Starting Date: November 1, 2005 . Ending Date: November 30, 2005

Section I. Accomplishments (*Please provide a bulleted list of project accomplishments as well as a description of their importance to the project.)*

***PROJECT OBJECTIVES***

The overall objective of this project is to develop cost-effective, high-temperature gas separation membranes for producing inexpensive, high-purity hydrogen ($H_2$) from synthesis gas generated by steam reforming or gasification of fossil fuels. The two specific technical objectives of the project are:

(i) To develop polymeric and/or polymer-based nanocomposite membranes with high $H_2$ permeability, high $H_2$/carbon monoxide (CO) and $H_2$/carbon dioxide ($CO_2$) selectivities, and high thermal stability up to 250-300 °C.

(ii) To demonstrate the technical and economic feasibility of using such membranes for producing low-cost fuel-cell-quality $H_2$ from synthesis gas streams.

***PROJECT ACTIVITIES AND STATUS***

The Grant Activities for the project consist of seven (7) tasks. The project accomplishments during this report period are summarized in the bulleted list below.

UT

- Membrane Permeation Testing: PBI samples prepared by RTI were evaluated for defects and permeability. Preliminary data for copper filled Ultem® 1000 has been obtained. ***(Project Task 2)***

RTI

- PBI Membrane Preparation: Preparation of free-standing, dense polybenzimidazole (PBI) composite films with Ni catalyst and silica nanoparticles continued using the new preparation protocol developed last month. Making good (defect-free) PBI nanocomposite membranes containing nanofiller particles is a critical step in the development of gas separation membranes for this project. ***(Project Task 1)***

- Membrane Permeation Testing: Evaluation of permeation data for unfilled PBI resin membranes, Samples #A5-M, #A6-1 and #A6-2M, were completed. Characterization of the stainless-steel-supported pure PBI composite (multilayered) membrane with pure $H_2$ was attempted. ***(Project Task 2)***

Specific results and details of this period's project activities are discussed on a task-by-task basis below.

**Indicate which part of the Grant Activities as defined in the grant agreement, the above accomplishments are related to:**

***TASK 1: Prepare High-Temperature Membranes***

UT

No new membranes have been prepared during the November reporting period.

RTI

Celazole® PBI (polybenzimidazole) nanocomposite membrane preparation was continued using 10-nm $SiO_2$ particles as well as $Ni/Al_2O_3$ catalyst nanoparticles. An 8-mil casting-knife gap was used to draw down the 10-wt%-silica- and 5-wt%-Ni-catalyst-doped PBI casting solutions onto glass plates. The cast films were immediately placed in a 70 °C oven with $N_2$ purge to dry for 24 h and then post-heat-treated at 300 °C for 2 h.

***TASK 2: Evaluate Membrane Permeation Properties***

UT

Two different types of materials have been tested for permeability and defects during this reporting period. First RTI had submitted a number of thin (< 15 µm thick) PBI films for permeability characterization. These films had extremely high permanent gas flux indicative of pinhole defects. A second, thicker set of PBI films have been received but not characterized during this reporting period.

The second type of material tested was Ultem® 1000 filled with 8.5 volume % copper nanoparticles. The copper had a reported surface area of 30 $m^2/g$ and a primary particle diameter of 25 nm. The sample thickness was over 200 µm thick, which was sufficiently thick to prevent the formation of trans-film defects. Permeability data are listed in Table 1. The $CO_2$ and $CH_4$ permeabilities increase while $H_2/CO_2$ and $CO_2/CH_4$ selectivities appear to decrease with the addition of Cu. Such behavior may indicate that the Cu reduces the size sieving capability of the polymer matrix, much like the $SiO_2$ reported earlier in this project.

**Table 1**. Copper filled Ultem® 1000

| Sample | Permeability [Penetrant size Å]$^2$ (Barrer) | | |
|---|---|---|---|
| | $H_2$ [2.89] | $CH_4$ [3.8] | $CO_2$ [3.3] |
| Ultem® 1000 | 9.4 | 0.03 | 3.3 |
| Ultem® 1000 w/ 8.5 vol. % copper | 8.1 | 0.12 | 8.9 |

RTI

Last month, efforts began on testing the trial PBI composite (multilayered) membrane cast on a Mott Corporation 316L stainless steel support with 0.5-µm pore size. Thin PBI layers had been deposited

onto the support substrate by knife-casting and manual coating/spreading of a PBI solution (14 wt% in DMAc). To test this multilayered PBI composite membrane, the permeation cell had to be changed to one that would hold the square support substrate. In the first trial of the stainless-steel-supported PBI composite membrane, large gas leaks were caused by poor O-ring sealing inside the cell. Addition of a second graphite O-ring allowed the desired 200 psig feed pressure to be maintained in the cell, but $H_2$ testing with GC analysis still indicated large defects in the PBI coating.

Previously, two host Celazole PBI membrane films (#A5 and #A6) were made by knife-casting with a 10-mil knife gap. Once cast, bulk drying of the films was completed at 70 °C under $N_2$ for 24 h. The films were then removed from the casting plates and placed back in the oven to post-dry at 300 °C under $N_2$ for 3 h to drive off residual solvent and moisture. Sample #A5-M, a masked PBI film with a thickness of ~13 μm and a 2.8-$cm^2$ permeation area, was tested to obtain pure-gas and syngas mixture permeation properties at 202 psig feed pressure and 98 °C (Table 2). Continued characterization of this film at different temperatures could not be completed because the membrane became defective upon further testing. From the host PBI film #A6, two samples, #A6-1 and #A6-2M, were cut. Sample #A6-1, a PBI resin film with ~30 μm thickness, was characterized at 98 °C and 202 psig feed pressure using pure gases and a three-component syngas mixture (Table 3). Unfortunately, upon completion of this first set of tests, the film cracked after being left in the permeation cell overnight.

**Table 2**. Permeability Data for PBI Membrane Sample #A5-M at 98 °C

| Gas | Permeability (barrer) | | | Selectivity | |
|---|---|---|---|---|---|
| | CO | $H_2$ | $CO_2$ | $H_2/CO_2$ | $H_2/CO$ |
| Pure gas | | | | | |
| *Pre-syngas* | — | 23 | 2.1 | 11 | — |
| *Post-syngas* | — | 17 | 2.2 | 7.7 | — |
| Syngas mixture[a] | 18[b] | 13 | 3.7 | 3.5 | 0.72[c] |

1 barrer ≡ $10^{-10}$ $cm^3$(STP)·cm/($cm^2$·s·cmHg)

Film thickness = 13 μm; Masked film area = 2.8 $cm^2$

Feed pressure = 202 psig; Permeate pressure = 0 psig
Downstream He sweep rate = 20 $cm^3$/min

[a] Sygas mixture composition: 12.48% $CO_2$, 36.78% $H_2$, and balance CO; Test stage-cut < 0.1%.

[b] Values computed using CO concentration obtained by manual integration of GC peak for CO.

[c] Selectivity less than unity was unexpected and may be due to larger than expected error in the GC CO concentration estimated manually.

**Table 3**. Permeability Data for PBI Membrane Sample #A6-1 at 98 °C

| Gas | Permeability (barrer) | | | Selectivity | |
|---|---|---|---|---|---|
| | CO | $H_2$ | $CO_2$ | $H_2/CO_2$ | $H_2/CO$ |
| Pure gas | | | | | |
| *Pre-syngas* | — | 9.8 | 0.8 | 12 | — |
| *Post-syngas* | — | 9.5 | 0.6 | 16 | — |
| Syngas mixture[a] | 0.25[b] | 10 | 3.1 | 3.2 | 40 |

1 barrer ≡ $10^{-10}$ $cm^3$(STP)·cm/($cm^2$·s·cmHg)

Film thickness = 30 μm; Masked film area = 2.8 $cm^2$

Feed pressure = 202 psig; Permeate pressure = 0 psig

Downstream He sweep rate = 20 $cm^3$/min

[a] Sygas mixture composition: 12.48% $CO_2$, 36.78% $H_2$, and balance CO; Test stage-cut < 0.1%.

[b] Values computed using CO concentration obtained by manual integration of GC peak for CO.

PBI Sample #A6-2M was masked to an area of 2.54 $cm^2$ and had a thickness of 30 μm. Sample #A6-2M was characterized over a temperature range of 100-250 °C at ~200 psig feed pressure with pure $H_2$ and $CO_2$ and a syngas mixture. Comparisons of the pure-and mixed-gas permeabilities and selectivities of Sample #A6-2M are presented in Figures 1a and 1b, respectively. Its permeation properties are also compared to the results obtained for PBI Sample #A4 in Figure 2 and PBI Sample #B2 in Figures 3 and 4.

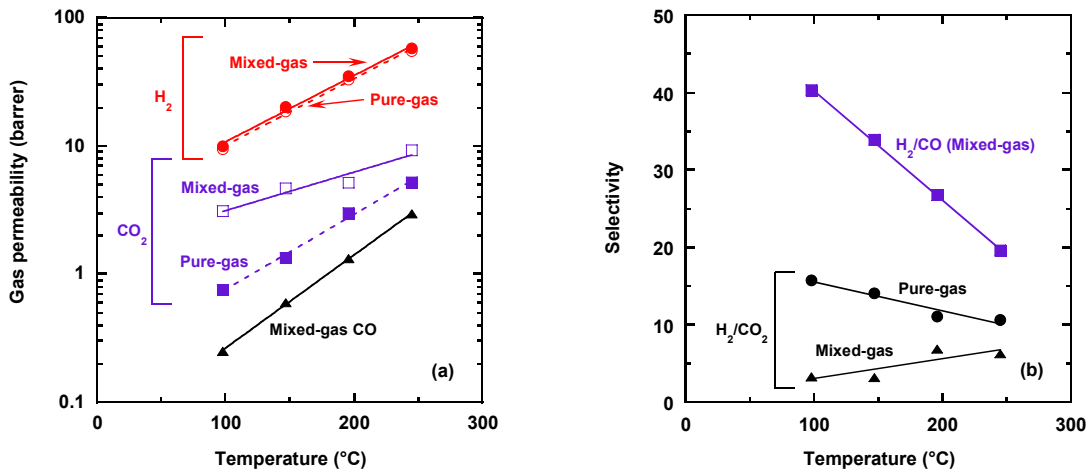


**Figure 1**. Effect of temperature on (a) $H_2$, $CO_2$, and CO permeabilities and (b) $H_2/CO_2$ and $H_2/CO$ selectivities of PBI Sample #A6-2M under pure- and mixed-gas conditions. Film thickness: 30 μm. Masked permeation area: 2.54 $cm^2$. Feed pressure: ~200 psig. Permeate pressure: 0 psig. Downstream He sweep rate: 20 $cm^3$/min. Syngas mixture composition used: 12.48% $CO_2$, 36.78% $H_2$, and balance CO. Stage-cut: <0.1% in mixed-gas tests. CO permeability values were computed from CO concentrations obtained by manual integration of GC peak areas. 1 barrer ≡ $10^{-10}$ $cm^3$(STP)·cm/($cm^2$·s·cmHg).

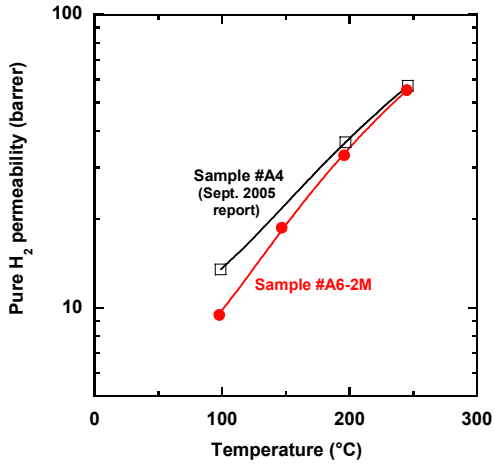


**Figure 2**. Comparison of the temperature dependence of pure $H_2$ permeability in pure PBI Samples #A6-2M and #A4. Sample #A6-2M has been described in Figure 1 caption. Sample #A4 data had been reported in the September 2005 status report for 21.5-μm-thick film. Feed pressure: ~200 psig. Permeate pressure: 0 psig. Permeate He sweep rate: 20 $cm^3$/min. 1 barrer ≡ $10^{-10}$ $cm^3$(STP)·cm/($cm^2$·s·cmHg).

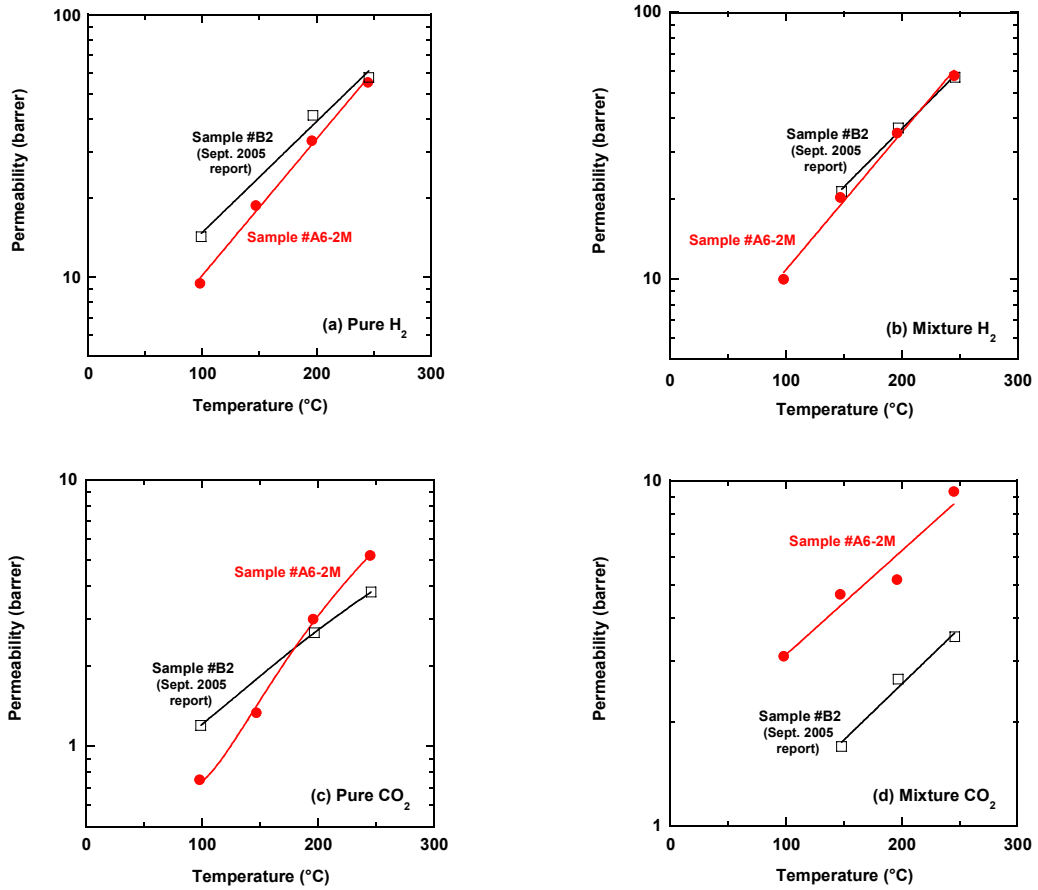


**Figure 3**. Comparison of the temperature dependence of pure- and mixed-gas permeabilities in pure PBI Samples #A6-2M and #B2: (a) pure $H_2$; (b) mixture $H_2$; (c) pure $CO_2$; and (d) mixture $CO_2$. Sample #A6-2M has been described in Figure 1 caption. Sample #B2 data had been reported in the September 2005 status report for ~35-μm-thick film. Feed pressure: ~200 psig. Permeate pressure: 0 psig. Permeate He sweep rate: 20 $cm^3$/min. Syngas mixture composition used: 12.48% $CO_2$, 36.78% $H_2$, and balance CO. Stage-cut: <0.1% in mixed-gas tests. 1 barrer ≡ $10^{-10}$ $cm^3$(STP)·cm/($cm^2$·s·cmHg).

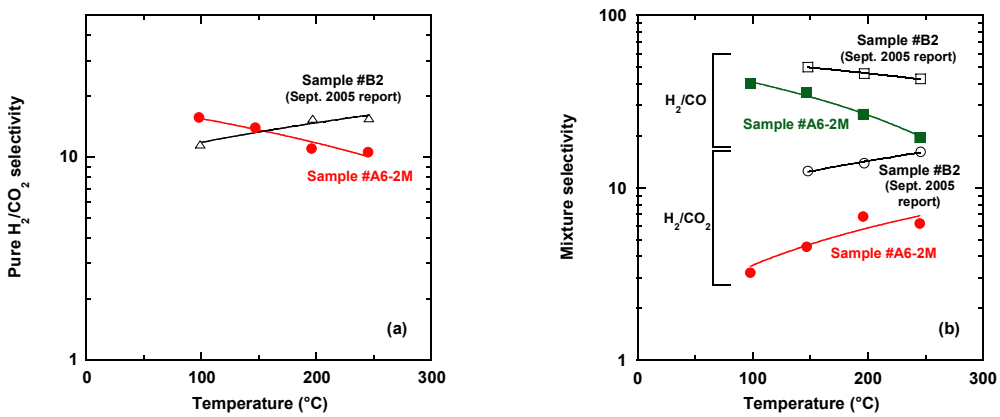


**Figure 4**. Comparison of the temperature dependence of (a) pure $H_2/CO_2$ selectivity and (b) mixture $H_2/CO_2$ and $H_2/CO$ selectivities in Samples #A6-2M and #B2. Sample #A6-2M has been described in Figure 1 caption. Sample #B2 data had been reported in the September 2005 status report for ~35-μm-thick film. Feed pressure: ~200 psig. Permeate pressure: 0 psig. Permeate He sweep rate: 20 $cm^3$/min. Syngas mixture composition used: 12.48% $CO_2$, 36.78% $H_2$, and balance CO. Stage-cut: <0.1% in mixed-gas tests.

***TASK 3: Evaluate Membrane Reactor Properties***

RTI

This task has not yet started at RTI.

***TASK 4: Characterize Thermal and Morphological Properties of Membranes***

UT

No thermal or morphological properties were measured this month.

RTI

No thermal or morphological properties were measured this month.

***TASK 5: Prepare Integrated System Process Design***

RTI

This task has not yet started at RTI.

***TASK 6: Perform Technical and Economic Analysis/Develop Commercialization Strategy***

RTI

This task is not yet scheduled to begin at RTI.

***TASK 7: Manage Project/Prepare Reports***

UT/RTI

The tenth monthly project report was prepared.

## Section II: Problems/Solutions

| | |
|---|---|
| Problem(s) Identified<br><br>(*Please report anticipated or unanticipated problem(s) encountered and its effect on the progress of the project)* | UT<br><br>No major problems were encountered this period.<br><br>RTI<br><br>No major problems were encountered this period. |
| Proposed Solution(s)<br><br>*(Please report any possible solution(s) to the problem(s) that were considered/encountered)* | UT<br><br>N/A this period.<br><br>RTI<br><br>N/A this period. |
| Action(s) Conducted and Results<br><br>*(Please describe the action(s) taken to resolve the problem(s) and its effect)* | UT<br><br>N/A this period.<br><br>RTI<br><br>N/A this period. |

## Section III. **Goals and Issues for Succeeding Period**: (*Please provide a brief description of the goal(s) you hope to realize in the coming period and identify any notable challenges that can be foreseen)*

UT

Dense films of Ultem® 1000 will be prepared 4 and 13 vol% copper and ready for testing in January, 2006. We will continue to characterize the permeability of the PBI samples that we have obtained from RTI.

RTI

Next period, we will continue characterization of the gas permeation properties of the pure PBI membranes and begin testing the PBI/nanoparticle nanocomposite films with pure $H_2$ and $CO_2$ and the syngas mixture as a function of feed pressure and/or temperature (up to 300 °C). Preparation of free-standing, dense PBI nanocomposite films will continue in order to cast successful silica and Ni catalyst-doped PBI membranes. Additionally, a second tubular AccuSep-supported PBI composite membrane module will be prepared by Pall Corporation and shipped to RTI.

Benny Freeman

_____. Date: December 12, 2005 .

*Authorized Project Representative's Signature*

**NOTE***: Please attach any additional information that you feel should be a part of your report or that may be required to meet the deliverable requirements for tasks completed during this reporting period.*