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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: April 5, 2005

Report for the **Monthly** period:

Starting Date: February 1, 2005 Ending Date: February 28, 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.

- A project kick-off meeting was held with Research Triangle Institute (RTI), our subcontract partner, at the University of Texas at Austin (UT) in Austin, TX, on February 24, 2005, to coordinate our research efforts on this project. Required attendees were Dr. Benny Freeman (Principal Investigator from UT), Mr. Scott Matteucci (UT graduate student), and Dr. Lora Toy (subcontract project leader from RTI). This kickoff meeting is important to the project because it provides necessary coordination between our efforts and those of our subcontractor so that we can make the most efficient progress possible toward project goals. ***(Project Task 7)***

UT

- Polymers and nanoparticles were acquired for this project from commercial sources. This accomplishment is important to the project because it provides the raw materials needed to prepare nanocomposite membranes for testing. ***(Project Task 1)***

- Nanocomposite membranes were successfully prepared from Ultem® 1000, which is a highly thermally stable polymer, and MgO nanoparticles. These nanocomposite membranes, containing

13 vol% MgO, were tested in pure-gas permeation studies. This accomplishment is important to the project because it identifies a new polymer matrix material, Ultem® 1000, which can be successfully prepared as a nanocomposite film. ***(Project Tasks 1-2)***

<u>RTI</u>

- Negotiations on an Agreement for PBI Polymer or Solution Use were initiated between RTI and Celanese Advanced Materials, Inc. (CAMI) so that raw PBI (polybenzimidazole) polymer powder can be purchased for the project. This agreement is expected to be fully executed by the next report period. The procurement of PBI is important because PBI is one of the key thermally stable polymers with attractive H_2 separation properties to be developed into useful membranes in this project. PBI membranes, with and without nanoparticles, will be the focus of membrane development work at RTI. ***(Project Task 1)***

- A high-pressure, stainless-steel, tubular membrane module housing and two thin-film PBI membranes supported on high-temperature AccuSep® sintered porous metal substrate tubes were ordered from Pall Corporation. Subsequent evaluation of the gas separation properties of these AccuSep-supported PBI composite (i.e., multilayer) membranes, which have not yet reached the commercialization stage, is an important first step for the project because it will provide a separation-performance reference point for a current state-of-the-art, supported, thin-film PBI membrane that is in a form readily packageable into a useful industrial membrane module with reasonably high surface area/volume ratio. Membrane performance data obtained from these AccuSep-supported PBI membrane tubes will guide our next research and development steps on how thin to make the selective PBI layer on microporous supports so that an optimal, practical combination of high H_2 selectivity and high H_2 productivity (flux) of this membrane can be attained. ***(Project Task 1)***

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

<u>UT</u>

During this period, several highly thermally stable polymers and appropriate inorganic particles were acquired for screening as high-temperature, hybrid inorganic/organic membrane materials. Table 1 and Table 2 provide a list of the materials that have been obtained for this research project.

Many attempts were made to solution-cast Torlon AI-10 filled with MgO and SiO_2 nanoparticles. Upon drying, these films became brittle and were prone to cracking before the drying step was complete. Fragility and the limited film formation ability of Torlon-based nanocomposites appear to be independent of filler type. Matrimid and Ultem® membranes will become the focus of the research going forward at UT. Nanocomposite films of Ultem® and MgO were successfully prepared, and their permeation properties are reported in Task 2 below.

Table 1. Highly Temperature-Resistant Candidate Membrane Polymers

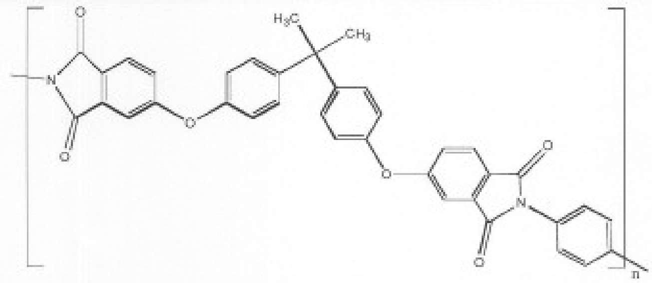
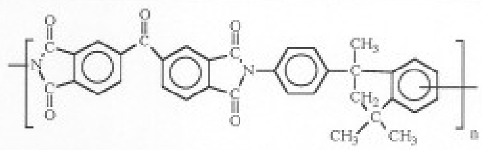
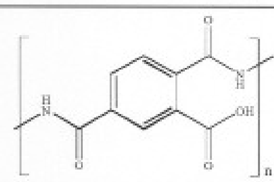
Polymer	T_g (°C)	Structure
Ultem® 1000	209	
Matrimid® 5218	338	
Torlon AI-10	272	

Table 2. Candidate Nanoparticle Materials

Nanoparticle type	Particle diameter (nm)	Expected particle reactivity
MgO	3	Neutral
SiO_2	10	Neutral
TiO_2	5	Neutral
Zn	20	WGS* catalyst
Ni	20	CO hydrogenation catalyst

* WGS ≡ water gas shift

RTI

Our subcontract partner, RTI, began negotiations on an Agreement for PBI Polymer or Solution Use with Celanese Advanced Materials, Inc. (CAMI) so that raw PBI (polybenzimidazole) polymer powder can be purchased for the project. PBI, which is a commercially available polymer, is solely supplied only by CAMI. Over the last 4-5 years, CAMI has restricted the market availability of PBI to the public and has required that purchasers of raw PBI sign a polymer use agreement to prevent any conflicts and/or competition with CAMI's own technology development interests in PBI. This agreement is expected to be fully executed by the next report period.

Additionally, for Task 1, a high-pressure, stainless-steel, tubular membrane module housing and two thin-film PBI membranes supported on high-temperature AccuSep sintered porous metal substrate tubes were ordered from Pall Corporation. These AccuSep-supported PBI membrane tubes will be a good first step toward demonstrating the proposed thin-film composite (multilayer) membrane approach as one method to increase the flux of high-temperature polymer membrane materials into a range suitable for commercial deployment. In this approach, a thermally stable, H_2-selective polymer layer (e.g., PBI) is deposited onto a microporous support substrate (e.g., AccuSep porous metal tube). The porous support gives mechanical strength and no resistance to gas permeation. The thin selective polymer layer is the rate-limiting step to permeation and performs the desired separation. In particular, the thin-film composite membrane method allows user-control over the polymer layer thickness deposited on the porous substrate and, hence, control over the gas flux of the overall multilayer membrane structure. These supported (composite) membranes are also in a form suitable for packaging into practical membrane module devices with moderately high surface area/volume ratio. The performance of these initial AccuSep-supported PBI membrane tubes will guide our next development steps on how thin to make the selective PBI layer on microporous supports so that the best combination of high H_2 selectivity and high H_2 productivity of this membrane can be obtained for the application of interest.

TASK 2: Evaluate Membrane Permeation Properties

UT

Hybrid inorganic/organic films were successfully solution-cast using Ultem® 1000 and 13 vol% MgO. Methylene chloride was the solvent. Permeation properties are shown in Table 3, and permeation properties for the neat (i.e., filler-free) film, as determined by Vu et al.,[1] are included for comparison. The permanent gas permeation in the MgO filled Ultem® film increases significantly as compared to the neat polymer.

Table 3. Preliminary Permeation Data for Filled Ultem® 1000

Sample	Permeability (Barrer)				
	He	O_2	N_2	CH_4	CO_2
Ultem® 1000[1]	—	0.38	0.05	0.04	1.45
Ultem® 1000 with 13 vol% MgO[a]	17.43	1.10	0.17	0.14	2.51

[a] Permeation data acquired by Shuichi Takahashi of UT.

Temperature: 35 °C; Pressure : 50 psig

[1] Vu, D. Q.; Koros, W. J.; Miller, S. J., "Mixed Matrix Membranes Using Carbon Molecular Sieves I. Preparation and Experimental Results", *Journal of Membrane Science* **2003**, *211*, 311-334.

RTI

No significant activities occurred for this task at RTI during this report period.

TASK 3: Evaluate Membrane Reactor Properties

RTI

This task is not yet scheduled to begin at RTI.

TASK 4: Characterize Thermal and Morphological Properties of Membranes

UT

No significant activities occurred for this task at UT during this report period.

RTI

No significant activities occurred for this task at RTI during this report period.

TASK 5: Prepare Integrated System Process Design

RTI

This task is not yet scheduled to begin 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 first monthly project report was prepared. A project coordination meeting was held in Austin, TX, on Thursday, February 24, 2005, with two representatives (Dr. Lora Toy and Mr. Tom Nelson) from RTI, our subcontracting partner on this project. At this meeting, we reviewed progress to date and set the research agenda for the coming period of work.

Section II: Problems/Solutions

Problem(s) Identified *(Please report anticipated or unanticipated problem(s) encountered and its effect on the progress of the project)*	<u>UT</u> We have not been successful in preparing nanocomposite films from Torlon polymer. It was anticipated that some of the proposed polymers might not be suitable for nanocomposite preparation; little is known about the fundamental reasons that a polymer will or will not form nanocomposites with a given particle type, so some Edisonian attempts to identify suitable polymer/particle pairs is inevitable. The project progress was not affected by this development because we had anticipated that this might be an issue to overcome. <u>RTI</u> No problems were encountered this period.
Proposed Solution(s) *(Please report any possible solution(s) to the problem(s) that were considered/encountered)*	<u>UT</u> We have successfully prepared nanocomposites from Ultem® polymer. Therefore, we will focus future membrane preparation (at UT) on Ultem and other polymers (i.e., we will not proceed further with Torlon). <u>RTI</u> N/A this period.
Action(s) Conducted and Results *(Please describe the action(s) taken to resolve the problem(s) and its effect)*	<u>UT</u> We focused our efforts on polymers other than Torlon to prepare nanocomposite samples. This action allowed us to successfully prepare nanocomposite films. <u>RTI</u> 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

We plan to continue testing the nanocomposite formation properties of the polymer and particles indicated above. As nanocomposites are prepared, we will characterize their structure and permeation properties, as indicated in the contract. We will continue to coordinate our work closely with that of our subcontractor to insure maximum progress on the project.

RTI

Next period, the high-temperature, high-pressure mixed-gas permeation system at RTI will be modified slightly for the tests to be performed in this project, and its operation validated with a membrane standard. As needed, mass flow controller(s) on the permeation system will also be calibrated with the appropriate gases. The online gas chromatograph (GC) connected to the permeation system will be checked for proper operation and calibrated with appropriate multicomponent gas mixture standards. Additionally, PBI polymer will be ordered once the polymer use agreement with CAMI has been approved and executed. When the PBI is received, neat (nanoparticle-free) and nanoparticle-doped PBI membranes will be prepared via solution-casting and tested as they are ready. When the membrane module housing and AccuSep-supported PBI membrane tubes are received from Pall Corporation, these tubular PBI membranes will be evaluated with a ternary syngas mixture of H_2, CO_2, and CO as a function of feed pressure and temperature (up to 250-300 °C).

Benny Freeman

Authorized Project Representative's Signature

Date: 4/5/05

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.*