Georgia Tech Sponsored Research

Project	E-19-X87
Project director	Rezac Mary
Research unit	Chem Engr
Title	ACS-PRF: Controlled Pyrolysis for Formation of Organic/Inorganic Composite
Project date	8/31/1998

E-19-X87
#1
(new)

Georgia Institute of Technology
School of Chemical Engineering

September 23, 1996

The Petroleum Research Fund
American Chemical Society
1155 Sixteenth Street, N.W.
Washington, DC 20036

RE: Annual Reports for Project 30235 - G5

Dear Sirs:

Please find enclosed:

- two (2) copies of the Report on Activity Assisted by Grant PRF - 30235-G5
- two (2) copies of the Personnel Statement for the above grant
- two (2) copies of the Financial Statement for this project

If you require any further information, please contact me.

Sincerely,

Mary E. Rezac
Assistant Professor

enclosures

School of Chemical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332-0100 U.S.A.
PHONE 404·894·
FAX 404·894·2866

PERSONNEL STATEMENT

PRF# 30235 - G5 REPORTING PERIOD 09-01-95 TO 08-31-96

GRANTEE INSTITUTION Georgia Institute of Technology

PRINCIPAL INVESTIGATOR(S) Mary E. Rezac

GRANT PROJECT TITLE Controlled Pyroloysis for the Formation of Organic/Inorganic Composite Membranes

List undergraduate, graduate, and postdoctoral co-workers receiving stipends under the above named grant: DO NOT list the principal investigator(s).

NAME	TITLE OR ACADEMIC APPOINTMENT	PREVIOUS EDUCATION AND DEGREES*	COUNTRY OF PERMANENT RESIDENCE	PERIOD OF SUPPORT (MONTHS)	PERCENT OF SUPPORT FROM PRF**	DEGREES RECEIVED (IF ANY) DURING REPORTING PERIOD
none during year 1						
because concurrent fellow-						
support was available.						

List other co-workers on grant project not directly supported with ACS-PRF funds:

NAME	SOURCE OF SUPPORT	DATES ASSOCIATED WITH GRANT PROJECT
N. Shannon Moore	Georgia Tech	9-01-95 to 8-31-96

***For graduate students, indicate the College or University attended prior to graduate work. For postdoctoral fellows, give the name of the Ph.D. granting institution.**

****(during the period stated in preceding column)**

Revised 8/96

E-19-X87
#2

PERSONNEL STATEMENT

PRF# 30235-G5 REPORTING PERIOD September 1, 1996 TO August 31, 1997

GRANTEE INSTITUTION Georgia Institute of Technology

PRINCIPAL INVESTIGATOR(S) Mary E. Rezac

GRANT PROJECT TITLE Controlled Pyrolysis for formation of Organic - Inorganic Composite Membranes.

List **undergraduate, graduate, and postdoctoral** co-workers receiving stipends under the above named grant: **DO NOT** list the principal investigator(s).

NAME	TITLE OR ACADEMIC APPOINTMENT	PREVIOUS EDUCATION AND DEGREES*	COUNTRY OF PERMANENT RESIDENCE	PERIOD OF SUPPORT (MONTHS)	PERCENT OF SUPPORT FROM PRF**	DEGREES RECEIVED (IF ANY) DURING REPORTING PERIOD
None						

List other co-workers on grant project not directly supported with ACS-PRF funds:

NAME	SOURCE OF SUPPORT	DATES ASSOCIATED WITH GRANT PROJECT
N. Shanan Moore	GIT Fellowship, EPA	9/1/96 - 8/31/97

*For graduate students, indicate the College or University attended prior to graduate work. For postdoctoral fellows, give the name of the Ph.D. granting institution.

**(during the period stated in preceding column)

Revised 8/97

E-19-X87
#3

Georgia Institute of Technology
School of Chemical Engineering

September 23, 1996

The Petroleum Research Fund
American Chemical Society
1155 Sixteenth Street, N.W.
Washington, DC 20036

RE: Annual Reports for Project 30235 - G5

Dear Sirs:

Please find enclosed:

- two (2) copies of the Report on Activity Assisted by Grant PRF - 30235-G5
- two (2) copies of the Personnel Statement for the above grant
- two (2) copies of the Financial Statement for this project

If you require any further information, please contact me.

Sincerely,

Mary E. Rezac
Assistant Professor

enclosures

School of Chemical Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332-0100 U.S.A.
PHONE 404·894·
FAX 404·894·2866

THE PETROLEUM RESEARCH FUND

REPORT ON ACTIVITY ASSISTED BY

GRANT, PRF # 30235-G5

Page 1 of 1 pages.

PREPARED BY

Dr. Mary E. Rezac

Georgia Institute of Technology

Date September 3, 1996

Please refer to instructions.

Fill in information requested above for each page.

The report heading, narrative, and all drawings must be prepared within the box.

Please submit one sharp, clear "original" and a copy (Xerox, carbon, etc.) for each page.

PRF 8/78 - 1

30235-G5 Controlled Pyrolysis for the Formation of Organic/Inorganic Composite Membranes

Mary E. Rezac, Georgia Institute of Technology

The major objective of this study is the development of thermally, chemically, and mechanically stable support structures suitable for the addition of a permselective polymeric separating layer. We have focused on an organic-modified inorganic substrate because of the inherently higher stabilities of such materials. The inorganic studied here is a microporous metal structure (8 μm pore sizes and 30% porosity). It has been modified by a thin, even layer of silicone rubber applied by dip coating. Dip coating results in a controlled reduction of pore sizes between 0 and 10,000Å. Following dip coating, the silicone rubber has been modified via a partial pyrolysis technique to enhance stability. Partial pyrolysis was conducted in a two-step process. First, the sample was heated to between 200°C and 400°C in an inert atmosphere (either N_2 or He). Then, air was applied at temperatures ranging from 200°C and 280°C, promoting silica and oxygen crosslinking to form silica. The properties of the resultant membranes were analyzed in terms of room-temperature permeation rates, thermogravemetric analysis, largest pore size, degree of crosslinking and thermo-mechanical behavior.

Room temperature permeability studies have shown that initial purge gas choice and temperature play the most significant role in the resultant membrane morphology. As temperature increases, both membrane pore size and permeability increase. The pressure normalized flux of nitrogen through the composite ranges from approximately 2 GPU for purge gas temperatures of 200°C to 15,000 GPU for temperatures approaching 400°C.[1] Thermogravemetric analysis has shown that an increase in purge gas temperature results in enhanced stability. Concurrently, swelling experiments have shown that the effective molecular weight between the chains decreases, indicating an enhanced silica content. Dynamic mechanical analysis supports the conclusion.

Future research will evaluated the relationship between pre- and post- pyrolyzed pore structure in the membranes and the influence of this morphology on membrane transport and stability.

1. 1 GPU = $\frac{10^{-6}\text{cm}^3(\text{STP})}{\text{cm}^2*\text{s}*\text{cmHg}}$

Instructions on Reverse Side

ACS-PRF FINANCIAL STATEMENT

PRF# 30235-G5 Inst. Ref.# E-19-X87 Period From: 9/1/95 To: 8/31/96

Balance Carried Forward from Last Reporting Period (for ***This*** or ***Previous*** Grant) 0

Total Payments Received from PRF During ***This*** Reporting Period $10,000.00

Stipends to:	
a. Principal Investigator (Summer Salary and Fringes)	4,999.57
b. Graduate Students/Fellows (including benefits)	
c. Undergraduate Students	
d. Postdoctoral Fellows (including benefits)	
e. Summer Research Fellowship Supplement	
f. Undergraduate Research Supplement	
g. Others (Specify)	
Tuition (Graduate Students)	
Materials and Supplies	1,971.41
Equipment	
Publication Costs	
Travel (Identify costs for field work, if any)	486.48
Other Expenses ***(Attach itemized list)***	
Departmental Allocation (if budgeted)	
Total Expenditures During Reporting Period	7,457.46

Balance on Hand at End of Period 2,542.54

This is to certify that the expenses reported herein were incurred for education and research in accord with the terms of the approved ACS-PRF grant-in-aid.

Mary Rezac
Name of Principal Investigator

David V. Welch David V. Welch
Financial Officer (typed name and Signature)

Georgia Institute of Technology
Grantee Institution

Director, Grants & Contracts Accounting
Official Title

(404) 894-1255
Contact Person/Telephone

(404) 894-2629
Telephone Date

****

DO NOT complete this section unless there is a balance in the grant account at the termination date of the current grant agreement. Indicate below how the grant balance will be liquidated.

_____ By refund of unspent and uncommitted funds. The check should be drawn to the order of American Chemical Society-The Petroleum Research Fund, and identified by the PRF grant number.

_____ By use in the completion of the grant project. We hereby request approval by the American Chemical Society of an extension of the grant agreement, without commitment of additional funds, until_____ (Period up to one year, renewable).

_____ By transfer of unspent funds to the investigator's new grant account, ACS-PRF#_____

****

Please submit to The Petroleum Research Fund, American Chemical Society
1155 Sixteenth Street, N.W., Washington, DC 20036 Telephone (202) 872-6092 8/96

E-19-X87
#4

Georgia Institute of Technology

School of Chemical Engineering
Atlanta, Georgia 30332-0100 U.S.A.
PHONE 404·894·
FAX 404·894·2866

September 18, 1997

The Petroleum Research Fund
American Chemical Society
1155 Sixteenth Street, N.W.
Washington, DC 20036

RE: Annual Reports for Project 30235 - G5

Dear Sirs:

Please find enclosed:

- two (2) copies of the Report on Activity Assisted by Grant PRF - 30235-G5
- two (2) copies of the Personnel Statement for the above grant
- two (2) copies of the Financial Statement for this project

There is a small remaining balance in the grant account at the termination date. I request approval by the American Chemical Society of an extension of the grant agreement, without commitment of additional funds, until August 31, 1998.

If you require any further information, please contact me.

Sincerely,

Original Signed by me.

Mary E. Rezac
Assistant Professor

enclosures

THE PETROLEUM RESEARCH FUND

REPORT ON ACTIVITY ASSISTED BY

GRANT, PRF # 30235-G5

Page 1 of 2 pages.

PREPARED BY

Mary E. Rezac

Georgia Institute of Technology

Date 9/19/97

Please refer to instructions.

Fill in information requested above for each page.

The report heading, narrative, and all drawings must be prepared within the box.

Please submit one sharp, clear "original" and a copy (Xerox, carbon, etc.) for each page.

PRF 8/78 - 1

30235-G5 Controlled Pyrolysis for the Formation of Organic/Inorganic Composite Membranes

Mary E. Rezac, Georgia Institute of Technology

The major objective of this study is the development of thermally, chemically, and mechanically stable support structures suitable for the addition of a permselective polymeric separating layer. Due to the inability of integrally skinned polymer support structures to maintain porosity at higher temperatures,[1] we have focused on preparation of an organic-modified inorganic substrate which has chemical, thermal, and mechanical stability.

The inorganic studied here is a microporous metal structure (8 μm pore sizes and 30% porosity). It has been modified by a thin, dense layer of silicone rubber applied by dip coating. Partial pyrolysis and oxidation was conducted in a two-step process. First, the sample was heated to between 200°C and 400°C in an inert nitrogen atmosphere. Then, air was applied at temperatures ranging from 200°C and 300°C, promoting an increase in the number of silicon to oxygen bonds. Complete conversion to silica is not attained; thus, an intermediate between an organic and an inorganic material results. The properties of bulk films were analyzed to determine the change in chemical structure with pyrolysis and oxidative conditions. Transport properties through the modified, composite membranes were analyzed at higher temperatures.

Analysis of amorphous, bulk films shows that as pyrolysis and oxidative conditions become more aggressive, the inorganic content increases and the organic content decreases. Elemental analysis confirms that the oxygen to silicon ratio increases as treatment temperatures are increased. Samples treated at a purge gas temperature of 200°C and an oxidative temperature of 260°C have an oxygen to silicon ratio of 1.5, while samples treated at the highest temperatures have an oxygen to silicon ratio of 1.8. The corresponding carbon contents drop to 18% and 10%, respectively, at these treatment conditions. This transformation from a purely organic material to an inorganic/organic composite is apparent from the sorption behavior of methanol into the solids. Untreated organics exhibit Henry's law-type sorption. As treatment conditions become more severe, a transformation to dual-mode behavior and ultimately to Langmuirian sorption is

THE PETROLEUM RESEARCH FUND

REPORT ON ACTIVITY ASSISTED BY

GRANT, PRF # 30235-G5

Page 2 of 2 pages.

PREPARED BY

Mary E. Rezac

Georgia Institute of Technology

Date 9/19/97

Please refer to instructions.

Fill in information requested above for each page.

The report heading, narrative, and all drawings must be prepared within the box.

Please submit one sharp, clear "original" and a copy (Xerox, carbon, etc.) for each page.

observed. Dynamic mechanical analysis and thermogravimetric data support these findings.

Gas transport through these modified composites is controlled by surface diffusion. Thus, resultant pore sizes are in the range of 10Å to 40Å.[2] Surface diffusion-controlled transport results in increases in flux with increasing differential pressure and a large, negative energy of activation, as can be seen in Figure 1.

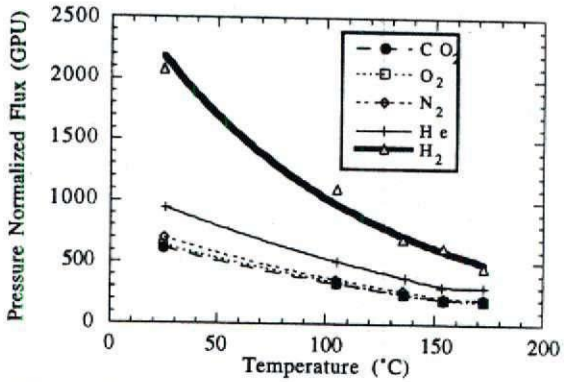

Figure 1: Transport through a composite membrane which has been treated at a pyrolysis temperature of 380°C and an oxidative temperature of 280°C. $\left(1\ \text{GPU} = \frac{10^{-6}\text{cm}^3(\text{STP})}{\text{cm}^2*\text{s}*\text{cmHg}}\right)$

Future research will evaluate composites after a thin, selective separating layer has been applied to the surface. Care must be taken to ensure that transport through the support structure is negligible when compared to that of separating layer at increased temperatures. Additional modifications to the polymer precursor in order to minimize this resistance will be explored.

References

1. Rezac, M. E., Moore, N. S., Back, A. Sep. Sci. Tech., (1997) 32, 505.

2. Way, J. D., Roberts, D. L. Sep. Sci. Tech., (1992) 27, 219.

E-19-X87
#5

Georgia Institute of Technology

School of Chemical Engineering
Atlanta, Georgia 30332-0100 U.S.A.
PHONE 404·894·
FAX 404·894·2866

February 16, 1999

The Petroleum Research Fund
American Chemical Society
1155 Sixteenth Street, N.W.
Washington, DC 20036

RE: Annual Reports for Project 30235 - G5

Dear Sirs:

Please find enclosed:

- two (2) copies of the Report on Activity Assisted by Grant PRF - 30235-G5
- two (2) copies of the Personnel Statement for the above grant
- two (2) copies of the Financial Statement for this project (I believe that this has also been forwarded under separate letterhead on February 5, 1999).
- One copy of a reprint resulting from this research.

If you require any further information, please contact me.

Sincerely,

Mary E. Rezac

Mary E. Rezac
Assistant Professor
(404) 894-1255
mary.rezac@che.gatech.edu

enclosures

THE PETROLEUM RESEARCH FUND

REPORT ON ACTIVITY ASSISTED BY

GRANT, PRF # 30235 - G5

Page 1 of 1 pages.

PREPARED BY

Mary E. Rezac

Georgia Institute of Technology

Date 2/1/99

Please refer to instructions.

Fill in information requested above for each page.

The report heading, narrative, and all drawings must be prepared within the box.

Please submit one sharp, clear "original" and a copy (Xerox, carbon, etc.) for each page.

PRF 8/78 - 1

30235-G5 Controlled Pyrolysis for the Formation of Organic/Inorganic Composite Membranes

Mary E. Rezac, Georgia Institute of Technology

The ultimate objective of this research is the development of thermally, chemically, and mechanically stable membrane capable of separating gases at elevated temperatures. The microporous substructure of integrally skinned polymeric membranes has been shown to collapse at elevated temperatures. This research focuses on the preparation of a hybrid organic/inorganic substrate with enhanced structural stability.

Silicone polymers have been evaluated for their ability to be partially transformed into silicon-containing hybrids. The majority of the research in this program focused on the performance of poly(dimethyl siloxane). Transformation from the organic to the inorganic was achieved by thermal pyrolysis in nitrogen or air. Results from this material indicated the following:

- Nanoporous materials with pores of less than 4 nm could be produced.
- The porosity is interconnected and traverses the sample thickness.
- The mechanical modulus of the hybrid materials are significantly higher than the virgin poly(dimethyl siloxane).
- The glass transition temperature increases by more than 150 C upon partial pyrolysis.

Analysis of the materials produced indicate that the relative oxygen to silicon ratio in the materials increase with the severity of the pyrolysis conditions. Solid-state NMR evaluation confirms a transformation from an $Si\text{-}O_2$- bonding to $Si\text{-}O_3$ and $Si\text{-}O_4$ configurations. Analysis of the evolved gases confirms that the predominant pyrolysis products are cyclic silicone trimers. Molecular modeling indicates that the pores formed result from the "condensation" of multiple oligomers to etch pores with diameters several times the molecular size of the evolved products.

Preliminary evaluation with siloxanes of alternative structures indicates that the diameters of the pores generated in this pyrolysis process are more strongly correlated with processing conditions than with the occupied volume of the evolved products.

Instructions on Reverse Side

ACS-PRF FINANCIAL STATEMENT

PRF# 30235-G5 Inst. Ref.# E-19-X87 Period From: 09/01/97 To: 08/31/98

Balance Carried Forward from Last Reporting Period (for *This* or *Previous* Grant) 6143.02

Total Payments Received from PRF During *This* Reporting Period 20,000.00

Stipends to:	
a. Principal Investigator (Summer Salary and Fringes)	
b. Graduate Students/Fellows (including benefits)	1041.66
c. Undergraduate Students	
d. Postdoctoral Fellows (including benefits)	
e. Summer Research Fellowship Supplement	
f. Others (Specify)	
Tuition (Graduate Students)	[illegible]
Materials and Supplies	[illegible]
Equipment	
Publication Costs	
Travel (Identify costs for field work, if any)	
Other Expenses *(Attach itemized list)*	
Departmental Allocation (if budgeted)	
Total Expenditures During Reporting Period	6143.02

Balance on Hand at End of Period .00

This is to certify that the expenses reported herein were incurred for education and research in accord with the terms of the approved ACS-PRF grant-in-aid.

Mary Rezac
Name of Principal Investigator

[signature]
Financial Officer (typed name and Signature)

Georgia Institute of Technology
Grantee Institution

Director, Grants and Contracts Accounting
Official Title

Davetta Thomas (404)385-0122
Contact Person/Telephone

(404)894-1026
Telephone

2/2/99
Date

****

DO NOT complete this section unless there is a balance in the grant account at the termination date of the current grant agreement. Indicate below how the grant balance will be liquidated.

_____ By refund of unspent and uncommitted funds. The check should be drawn to the order of American Chemical Society-The Petroleum Research Fund, and identified by the PRF grant number.

_____ By use in the completion of the grant project. We hereby request approval by the American Chemical Society of an extension of the grant agreement, without commitment of additional funds, until_____ (Period up to one year, renewable).

_____ By transfer of unspent funds to the investigator's new grant account, ACS-PRF#_____.

****

Please submit to The Petroleum Research Fund, American Chemical Society
1155 Sixteenth Street, N.W., Washington, DC 20036 Telephone (202) 872-6092 8/97

PERSONNEL STATEMENT

PRF# 30235 - G5 REPORTING PERIOD 09-01-97 TO 08-31-98

GRANTEE INSTITUTION Georgia Institute of Technology

PRINCIPAL INVESTIGATOR(S) Mary E. Rezac

GRANT PROJECT TITLE Controlled Pyrolysis for the Formation of Organic/Inorganic Composite Membranes

List **undergraduate, graduate, and postdoctoral** co-workers receiving stipends under the above named grant. Also list visiting faculty receiving a stipend from the Summer Research Fellowship supplement. **DO NOT** list the principal investigator(s).

NAME	TITLE OR ACADEMIC APPOINTMENT	PREVIOUS EDUCATION AND DEGREES*	COUNTRY OF PERMANENT RESIDENCE	PERIOD OF SUPPORT (MONTHS)	PERCENT OF SUPPORT FROM PRF**	DEGREES RECEIVED (IF ANY) DURING REPORTING PERIOD
Broderick Wilks	Grad. Student	BS ChE, 1996	USA	July - August	35%	none
		Clemson Univ.				

List other co-workers on grant project not directly supported with ACS-PRF funds:

NAME	SOURCE OF SUPPORT	DATES ASSOCIATED WITH GRANT PROJECT
N. Shanan Moore Stevens	Georgia Tech Fellowship	09/01/97 - 03/30/98 PhD Awarded 5/98
Charlene Harris, Undergrad Assistant	NONE	6/98 - 9/98

*For graduate students, indicate the College or University attended prior to graduate work. For postdoctoral fellows, give the name of the Ph.D. granting institution.

**(during the period stated in preceding column)

Revised 8/98

BIBLIOGRAPHIC INFORMATION

PRF# 30235 - G5

Please refer to instructions. Fill in information requested on each card. Type (double space) complete reference for one article in the space below:

PRINCIPAL INVESTIGATORS (S) Mary E. Rezac

Moore Stevens, N. S., REZAC, M. E.,
"Formation of hybrid organic/inorganic
composite membranes via partial pyrolysis
of poly(dimethyl siloxane)"
Chemical Engineering Science, (1998) 53, 1699.