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LOW COST HYDROGEN/NOVEL MEMBRANE TECHNOLOGY FOR HYDROGEN SEPARATION FROM SYNTHESIS GAS,

PHASE I

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A Quarterly Technical Progress Report
for the Period ending March 31, 1986

Contributors to this Report

R.W. Baker
K.-V. Peinemann
J.M. Mohr
I. Pinnau

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I. INTRODUCTION AND SUMMARY

This is the second quarterly technical progress report from Membrane Technology and Research, Inc. to the U.S. Department of Energy under contract number DE-AC21-85MC22130. This report covers the period 1 January 1986 to 31 March 1986. The goal of this program is to develop polymer membranes useful in the preparation of hydrogen from coal-derived synthesis gas.

During this quarter we began the first experiments aimed at developing high performance composite membranes for the separation of hydrogen from nitrogen and carbon monoxide. Three polymers have been selected as materials for these membranes: polyetherimide, cellulose acetate and ethylcellulose. This quarter we worked on polyetherimide and cellulose acetate membranes. The overall structure of these membranes is shown schematically in Figure 1. As shown, a microporous support membrane is first coated with a high flux intermediate layer then with an ultrathin permselective layer and finally, if necessary, a thin protective high flux layer.

II. PROGRESS THIS QUARTER

Task 3.1 Microporous Membranes

Our standard microporous support membrane is made from polysulfone (Udel® 1700) cast on a nonwoven polyester paper. We produce the polysulfone membrane on a routine basis using continuous membrane casting machines (12- and 40-inch wide). The average pore diameter of this support is 300 Å and the average nitrogen flux through this support is 1.5×10^{-2} $cm^3/cm^2 sec \cdot cmHg$. As far as pore size and permeability is concerned, the quality of this membrane is excellent. The disadvantage of using polysulfone is that it is attacked by many of the organic solvents in the polymer solutions used in subsequent coating operations. The polysulfone membrane does not change its properties after contact with alkanes or cycloalkhanes. But solvents such as acetone, ethyl acetate, toluene or dichloromethane alter the performance of the membranes. Sometimes these changes are barely visible but are nonetheless important. Table I shows the influence of acetone on a silicone coated polysulfone support. The membrane is not destroyed after treatment of the coated side of the membrane, but the gas flux decreases by almost an order of magnitude.

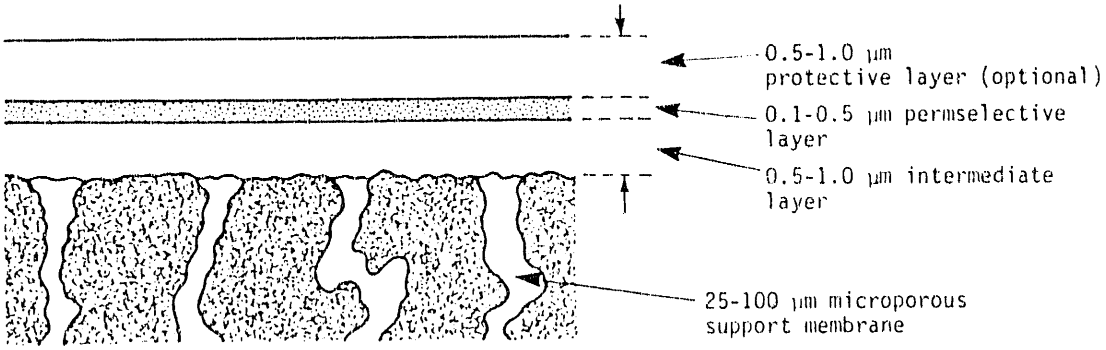

Figure 1. Composite hydrogen gas separation membrane.

Table I. Influence of Acetone Treatment on the Permeability of Silicone Rubber Coated Polysulfone

Membrane	P/ℓ_{N_2} (cm^3/cm^{2}sec·cmHg)	P/ℓ_{H_2} (cm^3/cm^{2}sec·cmHg)	α_{H_2/N_2} (-)
Polysulfone coated with one micron silicone rubber	2.8×10^{-4}	6.4×10^{-4}	2.3
As above, but acetone treated	1.3×10^{-5}	9.1×10^{-5}	7.0

More aggressive solvents such as toluene or dichloromethane destroy the polysulfone membrane completely even if the surface is coated with silicone rubber. To make more solvent resistant support membranes, membranes have been prepared from polyvinylidene fluoride (Kynar®), polyetherimide (Ultem®), and polyamide (Trogamid®). During the last two months we have focused our work on Trogamid. Trogamid-T is an amorphous polyamide soluble in dimethylacetamide (DMAc) and dimethylformamide (DMF). All membranes were cast on a nonwoven polyester (Kendall 1016) and immediately quenched in a water bath at 17°C. Table II shows some of the results obtained. We found that a polyamide concentration of more than 15% is necessary to obtain the uniform smooth surface required for subsequent coating operations.

Table II. Nitrogen Permeabilities of Trogamid Membranes

Solvent	Trogamid concentration (wt%)	Nitrogen flux through support membrane (cm^3/cm^{2}sec·cmHg)
DMAc	13	6.2×10^{-2}
	15	4.0×10^{-2}
	17	4.5×10^{-2}
	17.5	2.0×10^{-2}
DMF	13	7.0×10^{-2}
	15	2.8×10^{-2}
	17	5.5×10^{-3}
	17.5	1.5×10^{-3}

Using the support membrane made from 17.5 wt% Trogamid in DMAc, composite membranes with a defect-free layer of silicone 1.2 microns thick were prepared. Further experiments will be required to improve the reproducibility of this membrane.

Task 3.1(a). Polyetherimide Membranes

Integral asymmetric polyetherimide membranes were purchased from GKSS, a research company located in Hamburg, West Germany. The silicone coated membranes had an H_2/N_2 selectivity of more than 100 and a hydrogen flux of 7×10^{-5} $cm^3/cm^2sec\cdot cmHg$. A disadvantage of these membranes is that they are free standing, i.e. they are not cast on a support material. Consequently, they are relatively delicate and may not be capable of being rolled into spiral wound modules without damage. Polyetherimide membranes as thin film composites have been prepared and will be tailored to our application. Because the only suitable solvents for polyetherimide are chlorinated hydrocarbons, we are using Trogamid for the microporous support. Composites formed by Trogamid directly with polyetherimide have many defects, so we propose to overcome this problem by using a high permeability sealing layer between the polyetherimide and Trogamid layers. When silicone rubber was used as the sealing layer, it was found to be poorly wetted by the dichloroethane solutions used in the polyetherimide coating step. Subsequent experiments with Kraton, TPX , or combination silicone rubber/TPX as the sealing layer, yielded membranes with separation properties as shown in Table III.

Table III. Separation Properties of Polyetherimide Composite Membranes

Preparation procedure	Intermediate layer	Selective layer	Protective top layer	Hydrogen flux ($cm^3/(STP)cm^2sec\cdot cmHg$)	H_2/N_2
2x3% Kraton + 1x2% Polyetherimide in CH_2Cl_2	Kraton	polyetherimide	none	1.3×10^{-5}	11.4
	Kraton	polyetherimide	silicone	7.1×10^{-6}	86.0
1x2% silicone + 1x2% TPX + 1x2% polyetherimide	silicone/TPX	polyetherimide	none	2.4×10^{-5}	25.4
	silicone/TPX	polyetherimide	silicone	1.7×10^{-5}	81.0

Table III shows the best polyetherimide composites we have prepared up to now. The selectivity of these membranes is good, but further work will be needed to improve the hydrogen flux.

Task 3.1(b) Cellulose Diacetate Composites

We prepared two kinds of four-layer composites with cellulose diacetate as the selective layer:

polysulfone/silicone rubber/TPX/cellulose diacetate and
Trogamid/silicone rubber/TPX/cellulose acetate.

The additional TPX layer was necessary for two reasons: 1) because our preferred solvent for cellulose diacetate is acetone, with which TPX is much more wettable than silicone rubber, and 2) because acetone diffusion through the silicone rubber sealing layer attacks the Trogamid support and tightens the support membrane. The results obtained with these cellulose acetate membranes are shown in Table IV. These membranes are comparable in flux and selectivity with the best currently available cellulose acetate membranes. We believe even better membranes can be obtained with further work.

Table IV. Properties of our Ethylcellulose Diacetate Composites

Preparation procedure	Intermediate layer	Selective layer	Hydrogen flux ($cm^3/cm^2 sec \cdot cmHg$)	H_2/N_2
2x2% silicone +1x3% TPX +1x1% cellulose diacetate in acetone on Trogamid	silicone/TPX	cellulose diacetate	9.0×10^{-5}	27
1x2% silicone + 1x5% TPX +1x2% cellulose diacetate in acetone on Trogamid	silicone/TPX	cellulose diacetate	5.1×10^{-5}	30
2x2% silicone +1x2% TPX +2x1% cellulose diacetate in acetone on polysulfone	silicone/TPX	cellulose diacetate	4.5×10^{-5}	7.4
2x2% silicone +1x2% TPX +2x1% cellulose diacetate in acetone +1x2% silicone on polysulfone	silicone/TPX	cellulose acetate	4.4×10^{-5}	33.5

III. PLANS FOR THE NEXT QUARTER

During the next quarter we will focus our attention on membrane preparation in Task 3.1. In particular, we will complete the development of Trogamid solvent-resistant support membranes and the development of cellulose acetate and polyetherimide composite membranes. These membranes will then be evaluated, and their potential value as H_2/N_2 and H_2/CO separating systems will be assessed.

A subcontract covering the mathematical model studies in Task 4 has been negotiated with SRI International of Menlo Park. We will begin this work during the next quarter.

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