Proj. 22130.6.3
DOE/MC/22130-T10

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DOE/MC/22130--T10

DE92 017782

LOW COST HYDROGEN/NOVEL MEMBRANES TECHNOLOGY FOR HYDROGEN SEPARATION FROM SYNTHESIS GAS, PHASE I

Contract Number: DE-AC21-85MC22130

A Quarterly Technical Progress Report
for the Period ending June 30, 1987

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I. Introduction and Summary

This is the seventh quarterly technical progress report from Membrane Technology and Research, Inc. to the U.S. Department of Energy under contract number DE-AC21-85MC22130. The report covers the period 1 April - 30 June 1987.

During this quarter, we continued to work on the development of high-flux palladium-silver membranes for the separation of hydrogen from carbon dioxide. Palladium-silver/poly(etherimide) composite membranes were prepared by a vacuum sputtering technique. We investigated the influence of different poly(etherimide) support membranes on the performance of palladium-silver membranes. All membranes tested showed a hydrogen/carbon dioxide selectivity lower than that of the uncoated poly(etherimide)/poly(dimethylsiloxane) membranes. This is probably due to damage of the skin layer of the asymmetric poly(etherimide) support membranes during the palladium-silver electron bombardment.

Polysulfone/poly(dimethylsiloxane)/poly(ether-ester-amide) composite membranes were also prepared. Membrane samples consistently showed a carbon dioxide/hydrogen selectivity of 9 to 10 and a normalized carbon dioxide flux of 2 to 4 x 10^{-4} cm^3(STP)/ cm^2·sec·cmHg. These are extremely good values, superior to any commercially available membranes for this separation.

We continued to prepare polysulfone/poly(dimethylsiloxane)/poly(ether-ester-amide) crossflow spiral-wound modules with an effective membrane area of 2500-3750 cm^2. During the last quarter, we have substantially improved the design of our spiral-wound modules. The modules were tested with pure gases at feed pressures up to 100 psig and showed carbon dioxide/hydrogen selectivities of 7.5 to 9.5.

These results are encouraging and we believe that the polysulfone/poly(dimethylsiloxane)/poly(ether-ester-amide) modules are mechanically stable up to feed pressure of several hundred psig.

II. Progress This Quarter

Task 3.1 Preparation of Membranes

3.1.1 Palladium-Silver Membranes

Palladium-silver composite membranes were prepared in our laboratory using a vacuum sputtering technique. The membranes consist of a selective palladium-silver alloy layer deposited on an essentially defect-free asymmetric poly(etherimide) support membrane. The structure of the sputtered palladium-silver layer is very dependent on the surface structure of the support membrane. Therefore, the ideal support membrane would combine high gas flux with an essentially defect-free surface. Several asymmetric poly(etherimide) membranes were surface-modified to obtain support membranes that have the ideal properties described above. Table I summarizes the performance of surface-modified poly(etherimide) membranes.

Table I: Performance of Surface-Modified Poly(etherimide) Membranes for Hydrogen/Carbon Dioxide Separation

	Membrane	Surface Treatment	Normalized Flux ($cm^3(STP)/cm^2 \cdot sec \cdot cmHg$) H_2	CO_2	N_2	Selectivity H_2/N_2	H_2/CO_2
1)	Asymmetric poly(etherimide)	none	8.5×10^{-5}	1.7×10^{-5}	4.3×10^{-6}	20	5.0
2)	Asymmetric poly(etherimide)	acetone	6.5×10^{-5}	1.7×10^{-5}	9.2×10^{-7}	71	3.8
3)	Asymmetric poly(etherimide)	0.4% PMMA in acetone	5.5×10^{-5}	1.1×10^{-5}	3.2×10^{-7}	172	5.0

Defect-free poly(etherimide) membranes show a hydrogen/nitrogen selectivity of 200 and a hydrogen/carbon dioxide selectivity of 5.5. Thus, asymmetric poly(etherimide) membranes treated with a 0.4 wt% solution of poly(methyl methacrylate) in acetone can be considered defect-free. The surface-modified

poly(etherimide) membranes described in Table I were coated with thin palladium-silver layers using a vacuum sputtering technique. The permeation properties of surface-modified palladium-silver/poly(etherimide) composite membranes are given in Table II.

Table II. Performance of Surface-Modified Palladium-Silver/Poly(etherimide) Composite Membranes for Hydrogen/Carbon Dioxide Separation

	Membrane	Surface Treatment	Sputter Time (min)	Normalized Flux (cm^3(STP)/cm^2·sec·cmHg) H_2	CO_2	Selectivity H_2/CO_2
1)	Palladium-silver/ poly(etherimide)	none	0.25	2.5×10^{-5}	2.8×10^{-6}	8.9
			1.0	4.5×10^{-5}	1.1×10^{-5}	4.1
			2.0	7.1×10^{-5}	2.7×10^{-5}	2.6
			5.0	1.7×10^{-4}	5.0×10^{-5}	3.4
2)	Palladium-silver/ poly(etherimide)	acetone	0.25	3.2×10^{-5}	7.5×10^{-6}	4.3
			0.50	3.2×10^{-5}	9.2×10^{-6}	3.5
			5.0	2.8×10^{-4}	7.8×10^{-5}	3.6
3)	Palladium-silver/ poly(etherimide)	0.4% PMMA in acetone	0.5	2.4×10^{-5}	4.8×10^{-6}	5.0
			5.0	4.1×10^{-5}	1.5×10^{-5}	2.7

The best palladium-silver composite membrane showed a hydrogen/carbon dioxide selectivity of 8.9 and a normalized hydrogen flux of 2.5×10^{-5} cm^3(STP)/cm^2·sec·cmHg. This membrane was coated onto a non-treated poly(etherimide) support membrane. Unexpectedly, plasma-deposited palladium-silver layers onto surface-modified poly(etherimide) membranes showed hydrogen/carbon dioxide selectivities lower than those of uncoated asymmetric poly(etherimide) membranes. Table II shows that the performance of palladium-silver/poly(etherimide) membranes is very dependent on the sputter time. The membranes' hydrogen/carbon dioxide selectivities dropped and gas fluxes increased with increased sputter time. We assume that the skin layer of the asymmetric poly(etherimide) membrane is damaged by electron bombardment during the plasma deposition of the palladium-silver layer. Thus, it was not possible to prepare defect-free palladium-silver membranes in all experiments.

3.1.2 Poly(ether-ester-amide) Membranes

During the last quarter, we also optimized the coating procedure used to prepare polysulfone/poly(dimethylsiloxane)/poly(ether-ester-amide) composite membranes. Several rolls of poly(ether-ester-amide) composite membranes were made without any problems in reproducibility.

Table III summarizes the properties of two different poly(ether-ester-amide) membranes that were prepared during this report period.

Table III. Performance of Poly(ether-ester-amide) Composite Membranes for Carbon Dioxide/Hydrogen Separation

Membrane	Sample #	Normalized Flux ($cm^3(STP)/cm^2 sec \cdot cmHg$) H_2	Normalized Flux ($cm^3(STP)/cm^2 sec \cdot cmHg$) CO_2	Selectivity CO_2/H_2
I. Polysulfone/poly(dimethylsiloxane)/poly-(ether-ester-amide)	1	3.9×10^{-5}	4.2×10^{-4}	10.8
	2	4.3×10^{-5}	4.3×10^{-4}	10.0
	3	3.8×10^{-5}	4.0×10^{-4}	10.5
	5	3.7×10^{-5}	4.0×10^{-4}	10.9
	6	3.9×10^{-5}	4.2×10^{-4}	10.7
	7	4.4×10^{-5}	4.5×10^{-4}	10.3
	8	3.9×10^{-5}	4.1×10^{-4}	10.5
II. Polysulfone/poly(dimethylsiloxane)/poly-(ether-ester-amide)/poly(dimethylsiloxane)	1	4.8×10^{-5}	4.3×10^{-4}	9.0
	2	4.6×10^{-5}	4.3×10^{-4}	9.4
	3	4.8×10^{-5}	4.4×10^{-4}	9.2
	4	4.9×10^{-5}	4.4×10^{-4}	8.9
	5	4.7×10^{-5}	4.2×10^{-4}	9.0
	6	4.6×10^{-5}	4.4×10^{-4}	9.6
	7	5.0×10^{-5}	4.4×10^{-4}	8.8
	8	4.7×10^{-5}	4.3×10^{-4}	9.1

Membranes I and II were tested at 50 psig with pure gases at 25°C. Table I shows that both membranes had a normalized carbon dioxide flux of 4×10^{-4} $cm^3(STP)/cm^2 \cdot sec \cdot cmHg$. Membrane II showed a slightly lower carbon dioxide/hydrogen selectivity, attributable to the permeation resistance of the rather thick silicone top layer. However, a silicone top layer may be advantageous, since it serves to protect the thin, selective poly(ether-ester-amide) layer during the preparation of spiral-wound modules.

Task 3.2 Module Construction

Polysulfone/poly(dimethylsiloxane)/poly(ether-ester-amide) composite membranes were formed into small crossflow spiral-wound modules. A winding apparatus used to make these modules is shown schematically in Figure 1. As the first step in preparing a spiral-wound module, the membrane is cut to size and folded around the feed spacer material (usually polypropylene or polyethylene mesh) and the product distribution pipe. The membrane envelope is then moved to the wind-up machine. During the winding operation, the material is kept under a slight tension and the membrane is glued along the edges and ends. When the module is completely wound, a layer of reinforced tape is used to seal it. The module is then housed in an aluminum pressure vessel. A schematic of the crossflow spiral-wound modules produced at MTR is shown in Figure 2.

Several polysulfone/poly(dimethylsiloxane)/poly (ether-ester-amide) spiral-wound modules were evaluated with pure gases (N_2, CO_2 and H_2) at 25°C, as shown in Table IV.

Table IV. Performance of Polysulfone/Poly(dimethylsiloxane)/Poly(ether-ester-amide) Spiral-Wound Modules

Module #	Membrane Area [cm^2]	Feed Spacer	Permeate Spacer	Feed Pressure [psig]	Permeation Rate [cm^3(STP)/cmHg·sec] N_2	H_2	CO_2	Selectivity H_2/N_2	CO_2/N_2	CO_2/H_2
1	2500	A	A	10	0.018	0.115	1.13	6.3	62	9.9
				30	0.035	--	--	--	--	--
				50	0.084	0.420	2.23	5.1	27	5.3
2	2500	B	B	15	0.020	0.115	0.877	5.6	43	7.7
				30	0.020	0.115	0.880	5.5	42	7.6
				50	0.021	0.115	--	5.4	--	--
				80	0.021	--	--	--	--	--
				15	0.020	--	--	--	--	--
3	3750	A	B	10	0.015	0.087	0.780	5.9	53	8.9
				25	0.015	0.088	0.790	5.8	52	9.0
				50	0.016	0.089	0.840	5.7	54	9.5

Two different spacer materials were used as flow channels on the feed and permeate sides of the modules. Spacer material A is a polypropylene mesh with rather sharp edges and was used for module #1 on the feed and permeate side. We produced several modules of this type but the modules failed at feed pressures above 10 psig.

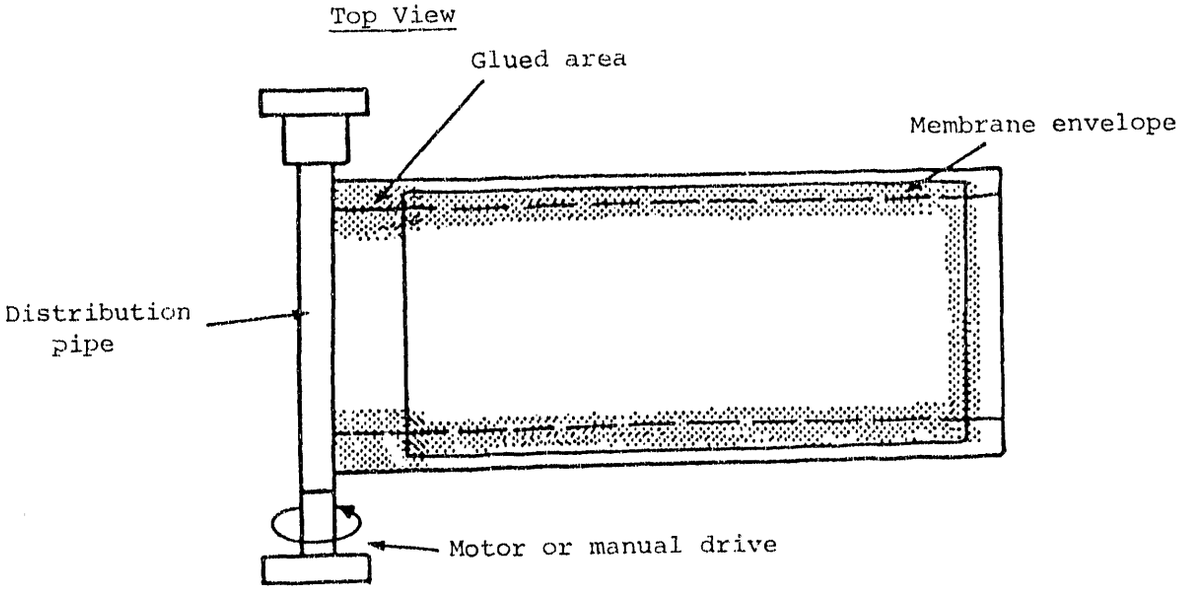

Figure 1. Module winding apparatus.

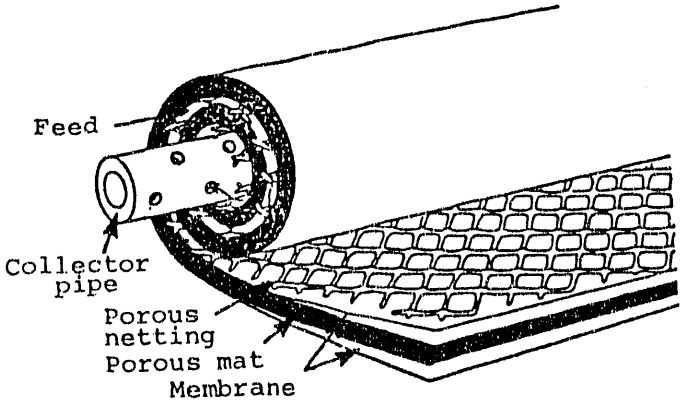

Figure 2. Schematic of a crossflow spiral-wound module.

Therefore, we have optimized our module design by preparing spiral-wound modules with a new spacer, material B. This new spacer is an extremely soft mesh with smooth edges. Several spiral-wound modules were prepared with spacer B on the permeate side and spacer A on the feed side, or spacer B on the feed and permeate sides. These modules showed improved mechanical stability, as shown in Table IV.

These results show that by choosing a smooth and soft spacer material, the ultrathin, selective poly(ether-ester-amide) layer is not destroyed during pressurization of the module.

III. Plans for the Next Quarter

During the next quarter, will prepare additional spiral-wound modules for the separation of carbon dioxide from hydrogen with an effective membrane area of 2500-5000 cm^2. These modules will be evaluated with pure gases (CO_2, N_2 and H_2) and carbon dioxide/hydrogen gas mixtures at feed pressures up to 200 psig.

We will start to prepare 40-inch-wide polysulfone/ poly(dimethylsiloxane)/poly(ether-ester-amide) composite membranes.

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